Rydberg States of Benzene in Rare-Gas Matrices

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In this paper we present experimental evidence for the observation of Rydberg states of benzene in solid Ar, Kr, and Xe. On the basis of semiquantitative theoretical evidence we argue that molecular Rydberg-type states of a guest molecule are amenable to experimental observation in rare-gas solids. These host matrices are characterized by a free electronlike conduction band, leading to a manifold of Wannier-type states. The electron–atom interaction in rare-gas solids is relatively weak so that the line broadening of these Rydberg-type states will not be excessive. The identification of these "Rydberg-type" states in a rare-gas solid is based on matrix shifts, vibrational structure, isotope effects, linewidths, and site splittings. Two Rydberg-type transitions of the benzene molecule were identified. From our analysis we conclude that: (a) The lowest ($n=1$) molecular Rydberg state in the rare-gas matrix can be correlated with the lowest Rydberg state in the gas phase, but is appreciably blue-shifted. The blue shifts are: 6000 cm^{-1} for Ar, 3150 cm^{-1} for Kr, and 1610 cm^{-1} for Xe. (b) The benzene Rydberg levels in the rare-gas matrix reveal some evidence for Jahn–Teller coupling effects, as is evident from the appearance of a nontotally symmetric vibrational component. (c) The linewidths observed for the Rydberg levels in the rare-gas matrix are qualitatively consistent with theory. (d) The second Rydberg transition in the rare-gas matrix is tentatively identified as corresponding to a $n=2$ Wannier state, which has no relation to the molecular levels of the isolated molecule. This assignment makes possible an estimate of the ionization potential of the molecule in rare-gas solids. (e) Our results provide evidence that the lowest molecular Rydberg state and molecular impurity Wannier states are amenable to experimental observation in rare-gas solids.

I. INTRODUCTION

Interest in electronically excited states of atoms and molecules trapped in inert matrices and in particular in rare-gas solids has steadily increased in the past decade.[1–12] From the available bulk of experimental data it can be safely concluded that the low-lying electronically excited states of the guest are only weakly perturbed by the surrounding rare-gas matrix. Alternatively, one may state that the intermolecular overlap between the wavefunction of the low-lying excited impurity state and the surrounding matrix is very small. We can thus safely conclude that these states can be adequately described within the framework of the tight-binding Heitler–London approximation, which implies that the impurity excited states have a unique parentage in the states of the isolated guest molecule. Small nonorthogonality corrections, medium shifts due to dispersion interactions, and lattice coupling effects are then introduced as second-order corrections. This description is analogous to Frenkel's exciton model for the lowest excited states of pure molecular solids.[13]

A radically different situation is encountered when the excited states of the impurity approach the bandgap of the host matrix, whereupon the tight-binding approach is not useful any more. When the impurity (or exciton) binding energy is small relative to the bandgap the Wannier model[14,15] constitutes an appropriate description of the physical situation. Because of dielectric screening the Coulomb electron–hole attraction is reduced, and when the radius of the excited state exceeds the lattice spacing the microscopic variation of the crystal and of the impurity core potential is averaged out. One can thus replace an atomic purity potential by a potential of the positive ion embedded in a uniform dielectric. Furthermore, when the conduction band is wide the crystal potential can

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[13] See, for example, A. S. Davydov, Usp. Fiz. Nauk **82**, 393 (1964) [Sov. Phys.–Usp. **6**, 145 (1964)].
[14] W. Kohn, Solid State Phys. **5**, 257 (1957).
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be subsummed into a renormalized effective mass m^*. The excited-state (one-electron) wavefunction $\Psi(\mathbf{r})$ can be then displayed as a superposition of Wannier states $a(\mathbf{r}-\mathbf{l})$,[14,15]

$$\Psi(\mathbf{r})=\sum_{\mathbf{l}} B(\mathbf{l})a(\mathbf{r}-\mathbf{l}), \quad (1)$$

where the vectors $\mathbf{l}$ label the lattice sites and $B(\mathbf{l})$ are the expansion coefficients. In the case of a slowly varying long-range potential $V(\mathbf{r})$, the (continuous) envelope function $B(\mathbf{r})$ is obtained from the effective mass equation[14,15]

$$\{\epsilon(i^{-1}\nabla)+[V(\mathbf{r})/\chi]\}B(\mathbf{r})=EB(\mathbf{r}), \quad (2)$$

where $\epsilon(\mathbf{k})$ is the dispersion curve for the conduction band and χ corresponds to the static dielectric constant of the medium. When the conduction band is parabolic, which is the situation for the rare-gas solids, the effective mass approximation reduces Eq. (2) to the simple form[14,15]

$$\{-(\hbar^2/2m^*)\nabla^2+[V(\mathbf{r})/\chi]\}B(\mathbf{r})=EB(\mathbf{r}). \quad (3)$$

In the case when a simple atomic ion core $V(R)=-e^2/r$ and the resulting energy levels are hydrogenic,

$$E_n=-G/n^2, \quad (4)$$

where $G=m^*e^4/2\chi^2\hbar^2$, while the oscillator strength varies as n^{-3}. The Wannier model was applied to shallow impurity states in n- and p-type semiconductors.[14] Recently attention was focused on deep impurity (and exciton) states in solid rare gases.[16–18] Experimental studies of the electronic states of solid rare gases and of rare-gas alloys led to the identification of Wannier states in these systems.[5–7] These optical measurements disclosed that the rare-gas atomic doublets $^1S_0\rightarrow{}^{3,1}P_1$ are located not far from the position expected for a $1s$ Wannier state,[19] while a new series of lines which appear in the solid[5–7] corresponds to a hydrogenic manifold of levels converging to the conduction band of the matrix.

The highly excited states of molecules in rare-gas solids are expected to reveal a similar behavior to the rare-gas alloys. In this context, molecular Rydberg states involving intershell transitions are of considerable interest. As it is well known, molecular Rydberg states of neutral molecules in the gas phase reveal an "atomiclike" behavior, whereupon the term values are described by a Rydberg formula and characterized by an appropriate quantum defect.[20]

The present work is devoted to an experimental study of the Rydberg states of benzene in rare-gas matrices. The questions we attempt to answer are as follows:

(a) Do Rydberg states exist in a dense medium? From the experimental point of view conflicting reports were recently presented. Atomic states such as the ^2P (e.g., the $1s\rightarrow 2p$ transition) of the hydrogen atom in Ar and Ne [8,9] and the ^3P and ^1P states of Xe in rare-gas alloys were unambiguously identified[6,7] so that one can safely conclude that the lowest atomic Rydberg states are amenable to experimental observation in a dense medium. The molecular Rydberg states of butadiene,[21] NO,[22] CH_3I,[23] ethylene,[24] and benzene[23] were reported to "disappear" (e.g., to be appreciably broadened) in the rare-gas matrices. On the other hand, experimental evidence for the observation of the lowest molecular Rydberg transitions in rare-gas matrices was presented by Milligan and Jacox for the CH_3 [11] radical and by Dressler for the NH_3 molecule.[12] Pysh, Rice, and Jortner[10] identified a Rydberg transition of acetylene in Ar and Kr and these results were recently confirmed by Katz and Jortner.[25] In the present work, experimental evidence for the identification of Rydberg states of benzene in rare-gas molecules is presented. A preliminary report of this work was published.[26]

(b) What is the relation between the Rydberg states of an isolated molecule and the Rydberg states of this molecule embedded in solid? The general theory of impurity states[14,15] will be useful to elucidate this problem.

(c) What are the relaxation mechanisms responsible for line broadening of molecular Rydberg states in solid matrices? Obviously if line broadening is drastic in the dense medium these states will not be amenable to experimental observation.

(d) What spectroscopic information can be obtained on the photoionization process of a guest molecule in a dense medium? This problem is of considerable interest in organic photochemistry since the pioneering work of Lewis.[27] Recent experiments by Albrecht and coworkers[28] demonstrated that photoionization can involve a two-photon process. Considering one-photon ionization of a guest molecule, the theory of impurity levels in semiconductors and in insulators is directly applicable. When the molecular Rydberg states are observed in the dense medium an approximate extrap-

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[22] J. Y. Roncin and N. Damary, Compt. Rend. **261**, 4697 (1967).
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[27] A. C. Albrecht and D. Lipkin, J. Am. Chem. Soc. **64**, 2801 (1942).
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olation procedure can be applied for the estimate of the molecular ionization potential in the dense medium.

II. MOLECULAR RYDBERG STATES IN RARE-GAS MATRICES

The gross features and Rydberg states of trapped molecules in solid matrices should be considered on the basis of the Wannier model for impurity states in the solid. The Coulomb correlation between the molecular positive ion core and the excited electron will result in large radius impurity states. Thus the problem of molecular Rydberg states in a dense medium is transferred from the field of molecular physics to the realm of solid-state physics. We should enquire at this point what are the guidelines for the identification of molecular Rydberg states in solid matrices? The following problems should be considered in this context.

A. Correlation Between the Lowest Rydberg Level in the Matrix and in the Gas Phase

The lowest molecular Rydberg level in the doped matrix corresponds to an intermediate case which cannot be adequately described neither in terms of the tight binding approximation nor by the Wannier model. From the point of view of the Wannier model the overlap of this excited state with the medium is not sufficiently large to make the dielectric screening and the effective mass approximation valid, and to neglect the repulsive contribution exerted by the ion core. Hence appreciable central cell corrections are introduced in this case.[14,17,18] An alternative description can be provided in terms of the tight-binding scheme,[29–32]

TABLE I. Matrix shifts of the lowest Rydberg state of atoms and molecules in rare-gas solids.

Host	Impurity	Δ (Matrix—vacuum)[a]	Reference
Ne	Xe	+0.65 eV	6
Ar	Xe	+0.79	6
Kr	Xe	+0.58	6
Ne	Kr	+0.59	6
Ar	Kr	+0.66	6
Ne	Ar	+0.88	6
Ar	H, D	+0.36	8, 9
Kr	C_2H_2	+0.52	10, 25
Ar	C_2H_2	+0.86	10
Kr	C_2H_4	+0.50	25

[a] Δ corresponds to the matrix shift.

[29] R. S. Knox, J. Phys. Chem. Solids **9**, 238, 265 (1959).
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[31] A. Gold, Phys. Rev. **124**, 1740 (1961).
[32] S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. **42**, 1907 (1965).

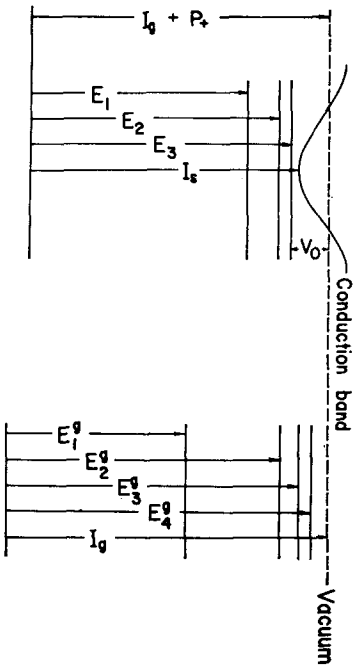

FIG. 1. A schematic energy-level diagram of the molecular Rydberg states in the gas phase and of the Wannier states of a molecular impurity in a solid. The lowest excitation E_1 in the solid corresponds to an intermediate case and can be roughly related to the gas-phase excitation E_{1g}. The excited states E_2, E_3, etc., correspond to legitimate Wannier states. Level splittings due to the charge distribution of the positive ion core and vibrational structure were not included.

whereupon the overlap of the wavefunction of this excited state with the medium is large, so that overlap orthogonality corrections will result in an appreciable blue spectral shift in the matrix relative to the location of this lowest Rydberg state in the isolated molecule. Whether this state is described in terms of a modified tight-binding scheme or in terms of a strongly perturbed Wannier model is just a matter of convenience. The data accumulated in Table I for the lowest atomic and molecular Rydberg states in rare-gas solids demonstrate that this blue spectral shift should be about ~0.5–0.8 eV and the effect of various rare-gas hosts will be in the order Ar > Kr > Xe.

B. The Location of Higher Rydberg Levels in the Doped Matrix

Higher "Rydberg-type" levels of an impurity molecule in the matrix are not expected to reveal any relation to the corresponding molecular states in the gas phase. These states can be indeed adequately described in terms of the Wannier model.[14,15] The spatial extension of the excited orbital will substantially reduce the contributions of core penetration and core orthogonality corrections which are important in the gas phase. On the other hand, corrections due to the deviations of the molecular core charge distribution

from a central charge[20] may still be of some importance. A series of quasihydrogenic levels should result, which converge to the bottom of the conduction band.

C. Vibration Structure

An important feature of the molecular Rydberg states in a dense matrix is the appearance of a vibrational progression which is close to the vibrational structure exhibited by the Rydberg states of the isolated molecule. This vibrational structure is essentially determined by the Franck–Condon vibrational overlap factors between the molecule in the ground state and the positive ion. This vibrational structure will not be seriously modified in the dense medium.

D. Relative Intensities

The theory of Wannier states[15] indicates that the relative intensities of molecular Rydberg states will fall off roughly as n^{-3}. As these lines are appreciably broadened (see Sec. II.F) the higher members of the series may not be amenable to experimental observation.

E. The Series Ionization Limit in the Matrix

We shall address ourselves again to the simple case whereupon the conduction band is free electronlike. As evident from Fig. 1, the photoionization threshold in the solid corresponds to the excitation of an electron from the impurity ground state to the bottom of the conduction band. This latter quantity is measured relative to the vacuum level and corresponds to the energy V_0 of an excess electron in the unperturbed solid. This quantity can be experimentally determined from adiabatic electron injection experiments,[33] or alternatively from photoemission data [see Eq. (6)]. The ground-state energy of the positive hole is determined by the classical polarization energy P_+. Hence the ionization potential I_s in the matrix is related to the gas-phase ionization potential I_g as follows:

$$I_s = I_g + P_+ + V_0. \tag{5}$$

The photoionization onset can be monitored by photoconductivity measurements. On the other hand, the photoemission onset F from the doped solid is given by

$$F = I_s - V_0 = I_g + P_+. \tag{6}$$

Now the higher molecular Rydberg levels in the solid are approximately given from Eq. (4) as

$$E_n \approx I_s - G/n^2. \tag{4'}$$

If these higher levels are detected, the simple energy-level formula can be used to estimate the value of I_s, and hence from Eq. (5) a reasonable estimate of $(P_+ + V_0)$ will be obtained. Finally, photoemission can be utilized to evaluate V_0 and P_+ separately.

F. Linewidths

An interesting feature exhibited by many molecular Rydberg transitions in the gas phase is that the absorption lines are rather narrow,[34] indicating that intramolecular electronic relaxation[35] is inefficient for these states in the isolated molecule. In a dense medium, molecular Rydberg states are expected to exhibit an appreciable line broadening. A semiquantitative theory developed by Rice and Jortner[36] is adequate for large-radius excited states. In large orbitals the bound state of the core–electron pair will be well defined provided that the electron mean free path exceeds the orbital circumference. Electron scattering by the host matrix will decrease the lifetime of the excited state, and provided that the scattering is frequent so that an orbit cannot be closed, no bound state can exist. This condition is equivalent to the requirement for cyclotron resonance, whereupon $\omega\tau < 1$ an orbit cannot be closed. Rice and Jortner[36] assumed that for large orbits the scattering of the electron is insensitive to the radius of curvature of the orbit, and the level broadening $\Delta\nu$ is expressed in the simple form[36]

$$\Delta\nu \sim (\pi\tau)^{-1}, \tag{7}$$

where τ is the relaxation time defining the mobility of the electron. The relaxation time can then be related to the structure factor of the system and to the Fourier transform of the scattering potential.[36] The latter quantity is radically different in the gas phase and in the dense medium due to polarization screening of the long-range electron–atom interactions. In view of these difficulties we have made use of the available electron mobility data in solid rare gases[37] ($\mu = 1000$ cm^2 V$^{-1}\cdot$sec^{-1} in Ar, $\mu = 3600$ cm^2 V$^{-1}\cdot$sec^{-1} in Kr, and $\mu \sim 4000$ cm^2 V$^{-1}\cdot$sec^{-1} in Xe). We expect from Eq. (7) that $\Delta\nu \propto \mu^{-1}$. Rough numerical estimates indicate that the linewidths corresponding to the higher excited Rydberg states should be of the order of ~ 100 cm^{-1}, and that the linewidths should be higher in solid Ar than in solid Kr and Xe. This analysis does not obviously apply to the lowest Rydberg level discussed in Sec. II.A, as only the higher Rydberg states can be handled by this scheme. In spite of the qualitative nature of this analysis we can conclude that in the rare-gas solids, electron–atom scattering is sufficiently weak, and although the higher molecular Rydberg states in the matrix are expected to be broadened, their width is not prohibitive for experimental detection.

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[33] Such experiments were performed on liquid rare gases. See, for example, M. A. Woolf and G. W. Rayfield, Phys. Rev. Letters **15**, 235 (1965).

[34] P. G. Wilkinson, Can. J. Phys. **34**, 596 (1956).

[35] See, for example, M. Bixon and J. Jortner, J. Chem. Phys. **46**, 715 (1968).

[36] S. A. Rice and J. Jortner, J. Chem. Phys. **44**, 4470 (1967).

[37] L. S. Miller, S. Howe, and W. E. Spear, Phys. Rev. **166**, 871 (1968).

We shall conclude this discussion by raising two experimentally pertinent points concerning the choice of the matrix for the observation of molecular Rydberg states and regarding the identification of these levels in a dense medium.

(a) The rare-gas solids constitute an ideal medium for the observation of molecular Rydberg states of host molecules because of the following reasons:

(1) The conduction band is free electronlike, and the large bandwidth (2–3 eV) makes the effective mass approximation applicable for the higher states.[16–18] Hence a manifold of Wannier-type states will result.

(2) The electron–atom interaction is weak so that the levels will not be "washed out" due to excessive line broadening.

It should be pointed out in this context that it will be apparently hopeless to look for these molecular Rydberg levels in mixed or pure crystals of organic molecules. In this case, the conduction band is narrow and far from being free electronlike, the effective mass approximation is not valid, and the electron scattering is strong as evident from the low mobility data.[38] Under these circumstances the molecular Rydberg states in these solids will be completely smeared out.

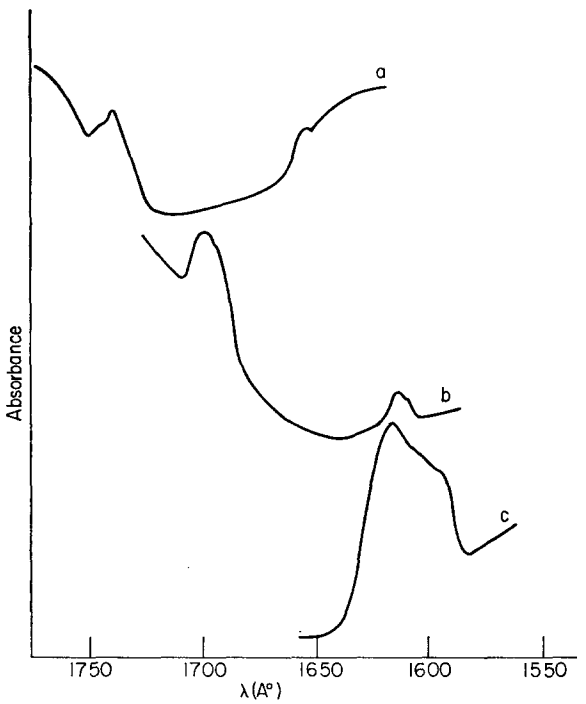

FIG. 2. The vacuum-uv absorption spectrum of benzene in solid rare gases. Samples were deposited at 20°K and photographed at 20°K. The microdensitometer tracings presented herein are not corrected for the energy dependence of the lamp intensity. (a) C_6H_6 in Xe, (b) C_6H_6 in Kr, (c) C_6H_6 in Ar.

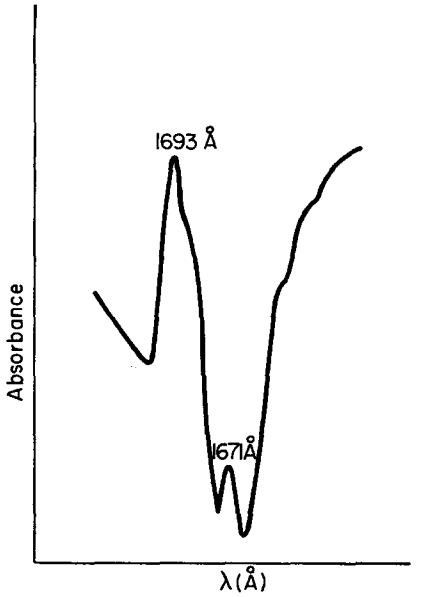

FIG. 3. The first Rydberg state of benzene in an annealed solid krypton matrix. Sample was deposited at 40°K and photographed at 20°K.

(b) The identification of the molecular Rydberg states in a matrix can be facilitated by the following observations:

(1) Matrix shifts: Blue spectral shift of the lowest Rydberg level in the matrix relative to the gas phase should result.

(2) Vibrational structure: should be reminiscent of the Rydberg transition in the free molecule.

(3) Substitution effects: Deuteration and chemical substitution shifts should be similar to those observed in the free molecule, as mainly the positive ion core is affected by these substitution effects.

(4) Photoconductivity and photoemission experiments in the doped matrix will yield pertinent information concerning the convergence limit of the Wannier series in the matrix.

III. EXPERIMENTAL DATA

The general experimental procedure was previously described.[26] The benzene–rare-gas mixtures (composition 1/100) were deposited at 20° and at 40°K. The spectra were photographed at 20°K, using Tanaka-type H_2, Xe, Kr, and Ar sources. The spectral range covered was 1200–1800 Å.

In Figs. 2 and 3 we display typical experimental results for the absorption spectra of benzene in solid Ar, Kr, and Xe. Experimental data pertaining to isotope effects and to matrix shifts are summarized in Tables II and III. Errors in the location of the band positions depend both on the width and on the intensities of the

[38] See, for example, O. H. Leblanc, Jr., in *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Labes, and A. Weissberger, Eds. (Interscience Publishers, Inc., New York, 1967), Vol. 3, p. 133.

TABLE II. Positions of the main Rydberg lines of benzene (C_6H_6) in rare-gas solids at 20°K.

	R_1		R_2	
Matrix	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})
Ar	1616	61 880	...	...
Kr	1694	59 030	1607	62 230
Xe	1739	57 500	1657	60 350

bands. In view of the appreciable line broadening, the positions of the lines are accurate within ±30 cm^{-1}.

Deposition of the benzene-h_6 samples at 20°K lead to the appearance of line splitting as evident from Fig. 2, while deposition at 40°K followed by measurement at 20°K appreciably reduced this fine structure, so that practically only a single main component was then observed. This behavior is analogous to that previously observed[39] for the $^1B_{2u}$ state and for the higher $^1B_{1u}$ and $^1E_{1u}$ transitions[26] of benzene in rare-gas matrices, and is clearly due to site splittings.

Some additional weak lines were observed on the high-energy side of the two main lines. This feature is demonstrated in Fig. 2.

IV. IDENTIFICATION OF THE BENZENE RYDBERG TRANSITIONS IN THE RARE-GAS MATRICES

The absorption of benzene in solid Ar, Kr, and Xe in the spectral range 1500–1750 Å reveals the following features:

(a) In solid Kr and Xe two main lines are observed, the lower-energy line is more intense by a factor of about 4:1. In solid Ar only the low-energy line could be identified.

(b) The splitting observed between the two main lines is 3195±60 cm^{-1} in Kr and 2850±60 cm^{-1} in Xe.

(c) The lines are rather broad in the solids. The linewidths of the lowest energy line are ~500±50 cm^{-1} in Ar ~200±30 cm^{-1} in Kr, and ~150±30 cm^{-1} in Xe.

These lines are assigned to Rydberg states of benzene in the rare-gas matrices on the basis of the following arguments:

A. Deuterium Isotope Shifts

The benzene Rydberg states in the gas phase reveal only a small deuteration shift. The ionization potential of C_6D_6 is higher than that of C_6H_6 by 33 cm^{-1}. The deuteration shifts for the lowest Rydberg states are[34]: 65 cm^{-1} for the *2Rooo* state[40] and 36 cm^{-1} for the *3Rooo* transition.[40] On the other hand, the deuteration shifts for $\pi\rightarrow\pi^*$ transitions in C_6H_6 relative to C_6D_6 are as follows: $^1B_{2u}$ (0–0) in the gas phase[41]: 200 cm^{-1}; $^1B_{1u}$ (0+606 cm^{-1}) in rare-gas matrices[26]: 150 cm^{-1}; and $^1E_{1u}$ (0–0) in rare-gas matrices[26]: 190 cm^{-1}. The deuteration shift of C_6D_6 relative to C_6H_6 observed for the two main lines in the Kr matrix is about 30 cm^{-1} for the 1694-Å transition and about 40 cm^{-1} for the 1606-A transition (Table II). Hence our assignment is consistent with the expected deuterium substitution shift for a Rydberg transition.

B. The Absence of False Vibrational Origins

On the basis of theoretical arguments and our previous experimental work the only $\pi\rightarrow\pi^*$ excitation which may be located in the spectral region under consideration can be the $^1E_{2g}$ state. Transitions to the $^1E_{2g}$ state should be induced by the 1037-cm^{-1} and by the 1485-cm^{-1} e_{1u} molecular vibrations with about the same efficiency so that two false origins separated by about 450 cm^{-1} are expected to appear in the spectrum.[42] In the annealed samples only single lines appear. Besides, the absence of a pronounced totally symmetric a_{1g} progression seems to be inconsistent with a $\pi\rightarrow\pi^*$ transition. The semiempirical calculations of Ross *et al.*[43] indicate that the Stokes shift along the a_{1g} normal coordinate is somewhat larger for the $^1E_{2g}$ state than for the $^1B_{2u}$ and the $^1B_{1u}$ $\pi\rightarrow\pi^*$ excited states of the benzene molecule. It is well known that the Franck–Condon vibrational overlap factor for the 0–0, 0–1, and 0–2 a_{1g} excitations (superimposed on the false vibrational origin) in the $^1B_{2u}$ state are about equal.[43] A similar behavior is expected for the $^1E_{2g}$ state.[43] Hence the assignment of these transitions to a $\pi\rightarrow\pi^*$ $^1A_{1g}\rightarrow{}^1E_{2g}$ excitation is unacceptable.

TABLE III. Isotope effect on the Rydberg states of C_6H_6 in a krypton matrix at 20°K.

	R_1		R_2	
Molecule	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})
C_6H_6	1694	59 030	1607	62 230
$C_6H_3D_3$	1693	59 070	...	...
C_6D_5H	1691	59 130	1604	62 340
C_6D_6	1693	59 070	1609	62 270

[39] Y. Diamant, R. M. Hexter, and O. Schnepp, J. Mol. Spectry. **18**, 158 (1965).

[40] We shall use the notation of Wilkinson (Ref. 34) for the benzene gas-phase Rydberg states.

[41] V. L. Broude, Sov. Phys.—Usp. **4**, 584 (1962).

[42] A. C. Albrecht, J. Chem. Phys. **33**, 169 (1959).

[43] For an estimate of Franck–Condon vibrational overlap integrals for the a_{1g} vibration in the $^1E_{2g}$ state see V. McCoy and I. G. Ross, Australian J. Chem. **15**, 573 (1962).

C. Linewidths

The observed linewidths are ~500 cm^{-1} in Ar, ~200 cm^{-1} in Kr, and ~150 cm^{-1} in Xe. These results are consistent with the order-of-magnitude estimates based on the theory of Rice and Jortner[36] (Sec. II). In particular, it is significant that the line broadening of the first transition in solid Ar is more severe than in Kr and in Xe. A similar behavior is observed for Wannier states in solid rare gases and in rare-gas alloys. The excessive line broadening in solid Ar provides a good excuse for our failure to observe the second Rydberg transition in this matrix.

The two main Rydberg lines do not correspond to vibronic components of the same electronic transition in the matrix. A spacing of ~3000 cm^{-1} can correspond only to a C–H vibration; however, the absence of deuterium isotope effects on this spacing rules out this possibility. A supporting evidence for this conclusion is obtained by consideration of the site splittings. When the samples are deposited at low temperature (20°K) the site splitting observed for the low-energy component is higher than that for the high-energy line. Thus in the Kr matrix the 1694 Å shows a site splitting of ~200 cm^{-1} while the 1607-Å line reveals a site splitting of ~70 cm^{-1}. On the other hand, the site splittings observed in the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ states of benzene are independent of the vibronic component within a given electronic configuration.[26,39] We may thus conclude that the two main lines observed in Kr and in Xe do not correspond to the same electronic transition.

We now turn our attention to the assignment of these two Rydberg transitions. The first Rydberg transition (1616 Å in Ar, 1694 Å in Kr, and 1739 A in Xe) is assigned to the lowest Rydberg state of benzene (*2Rooo* in Wilkinson's notation) which at the gas phase is located at 1789 Å. Our arguments supporting this assignment are as follows:

(a) Medium blue shifts: The matrix shifts of this line relative to the *2Rooo* state in the gas phase are 6000 cm^{-1} for Ar, 3150 cm^{-1} for Kr, and 1610 cm^{-1} for Xe. As discussed in Sec. II the lowest molecular Rydberg state in the matrix can be related to the corresponding strongly perturbed state in the isolated molecule. The matrix blue shifts observed for this level are consistent with the experimental data for the lowest Rydberg state of atomic impurities in doped solid rare gases. The order of the matrix shifts of the lowest Rydberg state in the three solids is consistent with the data displayed in Table I.

(b) Vibrational structure: The *2Rooo* benzene Rydberg state in the gas phase corresponds to a state of $^1E_{1u}$ symmetry (e.g., $e_{1g}\rightarrow p_z$ transition), as evident from the vibronic structure of this transition. This state undergoes dynamic Jahn–Teller coupling,[44] where the twofold degenerate electronic state is coupled to a doubly degenerate e_{2g} vibration.[45,46] A theoretical analysis[45] of the benzene Rydberg states in the gas phase reveals that the vibronic coupling strength is of the order of the vibrational frequency (606 cm^{-1}). Under these circumstances the Jahn–Teller coupling is exhibited in the spectrum by the appearance of a nontotally symmetric progression corresponding to the e_{2g} vibration, the strongest transition corresponds to the 0–0 band. The intensity of the 0–1 line should be about 10%–25% of the intensity of the 0–0 transition. Furthermore for this coupling strength the vibrational spacing between the 0–0 and the 0–1 line should be about 20% higher than the vibrational frequency (e.g., ~700 cm^{-1} for the 606-cm^{-1} vibration). These features are exhibited by the *2Rooo* Rydberg state in the isolated molecule.[34] Now the matrix effects on the Jahn–Teller coupling should be small, so that we expect that the transition in the matrix will exhibit a nontotally symmetric progression. Indeed, as evident from Fig. 3, a weak line separated by ~700 cm^{-1} from the main 1694-Å line is observed in annealed Kr matrix. The intensity ratio between this line and the 1694-Å line is of the order of 1:10. Hence this transition in the matrix reveals some evidence for a Jahn–Teller coupled state.

No experimental evidence for an a_{1g} progression was obtained. It should be pointed out that in the gas phase the 0–1 a_{1g} and the 0–1 e_{2g} vibrational components of the *2R* benzene Rydberg state have the same intensity.[34] It is thus puzzling why the a_{1g} progression was not experimentally observed. Some other weak lines were observed on the photographic plates; however, none of these could be assigned to the totally symmetric progression. Further work on this vibrational structure will be desirable.

We now proceed to consider the second Rydberg state in the matrix (1607 Å in Kr and 1657 Å in Xe). Two possibilities have to be considered:

(a) This state corresponds to the *2Rooo* Rydberg transition of the free molecule which is blue-shifted in the matrix. In this case, the Rydberg level in the matrix can still be correlated with the state of the free molecule. The spacing between the two Rydberg states observed in Kr and Xe is then assigned to the Liehr splitting.[20]

(b) This state corresponds to a higher Wannier state in the doped matrix, which is not related to molecular levels in the isolated molecule (see Sec. II).

The second possibility is preferred on the basis of the following (admittedly weak) considerations:

(i) The intensity ratio in the gas phase between the *2R'ooo* and the *2Rooo* transitions is about 1:50.

[44] H. C. Longuett-Higgins, V. Opick, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

[45] A. D. Liehr, Z. Naturforsch. **16a**, 641 (1961).

[46] B. Sharf, B. Honig, and J. Jortner, "Comments on the Vibronic Structure of Excited Electronic States" (unpublished).

Both in Kr and Xe matrices the intensity ratio between the first and the second "Rydberg" transitions is about 1:4. It is not plausible that the second Rydberg transition in these matrices corresponds to the perturbed $2R'ooo$ state.

(ii) The splitting between the $2R'ooo$ and the $2Rooo$ Rydberg states of benzene in the gas phase[34] is 3914 cm^{-1}. The splitting between the first and second transition in Kr and in Xe is about 3000 cm^{-1}. If the two excited states in the matrix were characterized by the same principle quantum number one would expect that the matrix environmental shifts of these two levels would be about equal. If the second Rydberg state in the matrix is assigned to the $2R'ooo$ level, the experimental data indicate that the environmental blue shift of this level is appreciably smaller than the matrix shift of the $2Rooo$ state in the dense medium.

(iii) The site splittings observed in unannealed samples are considerably larger for the first Rydberg state than for the second Rydberg level. It is thus unlikely that these two states correspond to a similar electronic configuration. The small site splitting of the second Rydberg state indicates that it corresponds to a highly excited state in the matrix, where the effect of short-range order in the matrix is small.

(iv) This assignment is consistent with the estimates of the ionization potential of the benzene molecule in rare-gas solids (see Sec. V). We thus tentatively assign the second Rydberg level in the matrix to a Wannier crystal state which has no relation to an excited molecular state.

A few comments concerning the labeling of these levels are now in order. Following the conventional assignment of Wannier states,[14,15] the lowest Rydberg level in the matrix can be assigned as the $n=1$ state, while the second Rydberg level should be assigned as the $n=2$ Wannier state. These principal quantum numbers refer to crystal states and do not correspond to the conventional assignment of molecular Rydberg levels in a free molecule[34] where the use of the principal quantum number is somewhat arbitrary. On the other hand, the assignment of the Wannier states is based on a central field potential. This approximation is sensible if we make use of Liehr's calculations which indicate that deviations of the molecular benzene ion core potential from spherical symmetry in the highly excited states in the matrix is quite small.

Some qualitative considerations are now in order. The size of the $n=2$ excited state is[14] $4\chi/m^*$ a.u., being of the order of $\sim$8 Å in Xe and in Kr. The orbit size exceeds the size of the trapped molecular positive ion (e.g., the hole). The coupling between the molecular ion and the electron is rather weak in view of the dielectric screening. Hence we can consider the hole to be produced in the $^2E_{1g}$ doubly degenerate state. This $^2E_{1g}$ degenerate state undergoes vibronic coupling by the e_{2g} molecular vibration.[44–46] Thus the resulting $n=2$ Wannier state is characterized by a hole which is subjected to Jahn–Teller coupling. The implications of this physical situation should be manifested in the appearance of a progression of the e_{2g} (606-cm^{-1}) vibration. Indeed, we were able to identify an additional weak band on the high-energy side of the 1604-Å band of benzene in krypton. This additional band is located at 1589 Å and the shift from the 0–0 $n=2$ Rydberg state is just 620 ± 50 cm^{-1}, as expected for a Jahn–Teller coupled 0–1 e_{2g} vibrational component.

V. THE IONIZATION POTENTIAL OF BENZENE IN RARE-GAS MATRICES

The tentative identification of the $n=2$ Wannier impurity states in benzene-doped rare-gas solids makes it possible to obtain some estimates for the ionization potential of this molecule in the solid matrices. The present approach is identical with the "optical" method used for shallow impurity states in semiconductors.[14] We shall add to the energy of the $n=2$ Wannier state the theoretically calculated energy of this state, which is just $G/4$ [see Eq. (4a)]. The relevant data for the solid rare gases obtained from Baldini's work[5–7] are displayed in Table IV. The I_s values for benzene in Xe and in Kr can be thus estimated. The result for Ar is just a rough guess, based on the assumption that the splitting between the first and the second (unobserved) Rydberg levels in the matrix is 3000 cm^{-1}. The values obtained for I_g–I_s are positive for all three solids (Table III). Inspection of Eq. (5) reveals that this result implies that $P_+ + V_0 < 0$. The polarization energy P_+ should be rather small (e.g., not exceed a fraction of an electron volt) in view of the large size of the positive ion. The values of V_0 in the solid rare gases are at present unknown. Theoretical and experimental data for *liquid* Ar demonstrate that $V_0 = -3000$ cm^{-1} in the liquid,[47] while the value for the corresponding solid

TABLE IV. Ionization potentials of the benzene molecule in rare-gas matrices.

Matrix	G^a (eV)	$m^{*\,b}$	χ^c	I_s (cm^{-1})	I_g–I_s (cm^{-1})
Ar	(2.1)	0.46 (0.43)	1.67	(69 000)	(6 000)
Kr	1.73	0.41 (0.46)	1.80	65 700	9 200
Xe	0.86	0.31 (0.54)	2.23	61 950	13 000

[a] G values from Refs. 5 and 6.
[b] Effective mass data from Refs. 17 and 18. Data in parentheses correspond to experimental data from Refs. 5–7.
[c] Dielectric constants from Ref. 5.

[47] J. Lekner, Phys. Rev. **158**, 130 (1967).

should not be appreciably different. Rough theoretical estimates based on the Wigner–Seitz model[48] indicate that for solid Ar and Xe, $V_0 \simeq -8000 - -12\,000$ cm^{-1}. This estimate is consistent with the analysis of our experimental data. To conclude this discussion we should point out that photoconductivity and photoemission experiments in the doped rare-gas solid will lead to independent information concerning the ionization potential of trapped molecules, and will provide a check on the present assignment of the energy levels in the doped rare-gas solids.

VI. DISCUSSION

In the present work we have advanced a number of semiquantitative criteria for the identification of Rydberg levels (or rather Wannier states) of guest molecules in rare-gas solids. Our semiquantitative theoretical arguments provide a satisfactory explanation under what circumstances molecular Rydberg-type states can be expected to "exist" in solids. Molecular Rydberg-type states are amenable to experimental observation in host matrices where the conduction band is free electronlike and where the electron–atom interaction is relatively weak. Thus the rare-gas solids constitute an ideal hot matrix for the observation of molecular Rydberg-type states of a trapped molecule. On the other hand molecular Rydberg-type states are expected to be smeared out (due to excessive line broadening) in organic crystals where the conduction band is narrow and where electron–molecule interaction is strong. These theoretical arguments were then immediately applied for the identification of the Rydberg states of the benzene molecule in rare-gas solids.

It is our opinion that from the experimental point of view the present work provides an unambiguous experimental evidence for the observation molecular "Rydberg-type" states in doped solid rare gases. These results combined with the previously reported data for the Rydberg states of acetylene[10,25] and of ethylene[25] in rare-gas matrices settle the old problem whether molecular Rydberg states do "exist" in solids. These experimental data are consistent with our theoretical arguments that molecular Rydberg states are amenable to experimental observation in rare-gas solids. The failure to observe Rydberg states in organic crystals is also explained by our theoretical considerations.

The theoretical discussion of molecular Rydberg-type levels in rare-gas solids should be obviously considered as preliminary as the following problems have to be treated in detail:

(a) In the higher ($n=2$) Wannier state the effect of the charge distribution in the molecular ion core[20] has to be investigated in detail.

(b) The theoretical evaluation of the spectral blue shifts in the lowest ($n=1$) molecular Rydberg state in rare-gas matrices is a difficult task. Early work by Knox and Gold[29,30] demonstrated the complications encountered in the divergence of the Löwdin symmetric orthogonalization procedure. The application of the Schmidt method[31] led to somewhat better results. A way out of this difficulty is to apply the pseudopotential description of the intermediate impurity state, and then to use a model Hamiltonian for actual calculations. Such a method was considered by Webber *et al.*[32] Recently, Harmanson and Phillips[17,18] have presented an elegant pseudopotential theory of atomic impurity (and exciton) states in solid rare gases. The extension of this treatment to molecular impurity states will be valuable.

The impurity states considered herein are located below the direct transition to the conduction band. Excited states above the conduction band threshold are expected to reveal interference effects between resonance and potential scattering, resulting in Fano-type antiresonance.[49] We have previously reported[26] that while using a continuous light source we were unable to observe the "antiresonances" reported by Pysh, Rice, and Jortner[10] in the benzene-doped rare-gas matrices in the region 1600–1200 Å. Obviously, electronic excitations of the impurity molecule which promote an electron from the highest filled MO (e.g., resulting in the molecular ion in its ground electronic state) will be located below the conduction band. However, excitations are also possible from lower-lying valence orbitals. These will result in an electronically excited positive ion core. Such states will overlap the conduction band states and will reveal interference effects which will be manifested in the absorption line shapes.

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[49] U. Fano, Phys. Rev. **124**, 1866 (1961).