THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 9 1 NOVEMBER 1965

Molecular Rydberg Transitions in Rare-Gas Matrices—Evidence for Interaction Between Impurity States and Crystal States

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(Received 12 July 1965)

As a first step in characterizing molecular Rydberg states in the solid state, the absorption spectra arising from acetylene and benzene impurity states in solid krypton and argon in the far-ultraviolet region have been obtained. The first member of the acetylene Rydberg series, which appears at 8.155 eV in the gas phase, is observed to be shifted to 8.67 eV in a krypton matrix and to 9.01 eV in an argon matrix. These large energy shifts are discussed, particularly with reference to the optical spectra of rare-gas solids and rare-gas alloys, where similar large blue shifts are observed. The far-ultraviolet spectra of benzene trapped in krypton and argon matrices show a qualitatively different phenomenon. The Rydberg states of benzene are observed to interact with conduction-band continuum states to exhibit anomalous Fano-type line shapes. The Rydberg states repulse the neighboring continuum states to produce sharp decreases in the continuum absorption intensity. These results are discussed in connection with other systems which show Fano-type line shapes.

I. INTRODUCTION

STUDY of environmental effects on atomic and molecular energy levels meant, until recently, measuring solvent shifts in solution. The information obtained through such experiments is seriously limited, however, by the general lack of knowledge of the properties of the liquid state. Particularly when the solvent has a permanent dipole moment, one does not know how to treat formally the interaction of the solute and solvent molecules in solution. The physical situation is improved when an ordered environment is used in place of a liquid. One can then take advantage of general considerations which apply to systems possessing translational symmetry. If, in addition, the matrix consists of weakly interacting molecules, one can focus attention on the interactions of interest—those between the solute and matrix.

Solid rare-gas matrices were used by Pimentel in a series of infrared optical experiments directed at studying unstable species and vibrational perturbations.[1] Later, McCarty and Robinson studied perturbations of low-lying electronic states of Hg, NH, and C_2 in the visible and near-ultraviolet regions,[2] and Pollack and Broida have studied the near-ultraviolet absorption spectrum of NO in crystalline and liquid krypton.[3] Schnepp has observed Mn and Mg transitions in solid rare-gas films,[4] and Weyhmann and Pipkin have reported the optical-absorption spectra of alkali atoms in rare-gas matrices.[5]

From the results of all these experiments, it is clear that low-lying electronic states are not strongly affected by the presence of a surrounding solid rare-gas matrix, aside from the removal of degeneracies by the matrix field. Inert-gas atoms do not interact strongly with a foreign electron, and the first excited state of the rare-gas atoms lies at least 8 eV above a tightly bound, closed-shell ground state. Alternatively, one may say that the overlap between the wavefunction of the low-lying impurity state and the wavefunction for the surrounding matrix will be very small.

A different situation holds when the excited state of the impurity is near the energy of the excited states of the matrix, since in that case the interaction will be large. Undoubtedly, one reason for the lack of theoretical work in the past has been the paucity of data, which arises from the experimental difficulty of combining cryogenic techniques with vacuum-ultraviolet spectroscopy. Nevertheless, the vacuum-ultraviolet region has become accessible enough for several important experiments to have been performed. Schnepp and Dressler have measured the spectrum of solid O_2 in the region from 2000 to 1550 Å[6] and Brith and Schnepp have measured the spectra of CO and N_2 in the region from 1600 to 1300 Å.[7] But the most interesting recent experiments, from the theoretical standpoint, have been those of Baldini on rare-gas solids and rare-gas alloys.[8]

Rare-gas alloys and pure rare-gas solids represent systems in which the lowest transition energy of each molecule is comparable to the energy of the lowest matrix transition. Baldini's results show the rare-gas atomic doublets ${}^1S_0\rightarrow{}^{3,1}P_1$ shifted to higher energies by

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[1] E. Whittle, D. A. Dows, and G. C. Pimentel, J. Chem. Phys. **22,** 1943 (1954); E. D. Becker and G. C. Pimentel, *ibid.* **25,** 224 (1956); E. D. Becker, G. C. Pimentel, and M. Van Thiel, *ibid.* **26,** 145 (1957); G. E. Ewing and G. C. Pimentel, *ibid.* **35,** 925 (1961); G. E. Leroi, G. E. Ewing, and G. C. Pimentel, *ibid.* **40,** 2298 (1964).

[2] M. McCarty and G. Robinson, Mol. Phys. **2,** 415 (1959).

[3] G. Pollack and H. Broida, J. Chem. Phys. **38,** 2012 (1963).

[4] O. Schnepp, J. Phys. Chem. Solids **17,** 188 (1960).

[5] W. Weymann and F. Pipkin, Phys. Rev. **137,** A490 (1965).

[6] O. Schnepp and K. Dressler, J. Chem. Phys. **42,** 2482 (1965).

[7] M. Brith and O. Schnepp (personal communication).

[8] G. Baldini, Phys. Rev. **128,** 1562 (1962); **137,** A508 (1965).

as much as 0.9 eV relative to the gas phase.[8,9] In addition, a new series of lines appears which represents transitions involving loosely bound electron–hole pairs with a hydrogenic manifold of energy levels converging to the conduction band of the matrix. At higher energies, beyond the threshold of the conduction band, annealed samples show several broad absorption peaks separated by rather sharp V-shaped troughs.

Until recently, crystal excitations were referred to as either Frenkel or Wannier excitons, according to which description was most nearly valid. The lowest excited states of crystals of aromatic molecules, for example, are often adequately described as Frenkel exciton states.[10,11] Rare-gas solids, however, represent an intermediate case in which the overlap of the wavefunction of the first excited state with the medium is large, but not large enough to make valid a dielectric screening approximation.

The case of a molecule excited to a Rydberg state within a rare-gas matrix is similar. First, molecular Rydberg states are atomiclike in the sense that the manifold of energy levels is hydrogenic. But more specifically, since the excitation energy is large and comparable to the excitation energy of the surrounding atoms, it also represents an *intermediate* exciton. It was with this background that the experiments described herein were undertaken, and it was hoped that evidence would be found for configuration mixing of crystal states and states of free molecule parentage.

II. EXPERIMENTAL PROCEDURE

The experimental procedure is largely based on the early work of Baldini[8] and Schnepp and Dressler.[6] Spectra were taken using a 1-m vacuum-ultraviolet scanning monochromator. The gratings used were ruled with 1200 or 600 line/mm with dispersions of 8.3 and 16.6 Å/mm, respectively. The ultimate resolution of the instrument is approximately 0.3 Å. Under the conditions of the experiment the resolution was approximately 1.0 to 2.0 Å.

A capillary-discharge light source, operated with hydrogen, provided a line spectrum in the range of this experiment: from 1650 Å to the onset of absorption by the lithium fluoride windows at 1050 Å. The hydrogen was pumped through the monochromator; the pressure in the chamber was approximately 5×10^{-4} mm Hg.

Gas mixtures were prepared in a glass vacuum line and transferred through stainless-steel tubing directly onto a sapphire window coated with the phosphor, sodium salicylate. The sapphire window was in thermal contact with a copper rod soldered to the bottom of a liquid-helium cryostat. Ultraviolet radiation was absorbed by the sodium salicylate and converted to visible radiation which was detected by a phototube (E.M.I. 9514B). The temperature was measured with a germanium resistance thermometer which was cemented to the sapphire window with Devcon epoxy glue.

Argon was obtained from a commercial source with a purity of 99.995%. The krypton which was used had been previously purified in this laboratory; its purity is estimated to be equal to that of the argon. Commercial acetylene was obtained with a purity of 99.6% and Spectrograde benzene was obtained from the Eastman Chemical Company. During the sample preparation, the gases were passed through a charcoal trap which was at room temperature for acetylene, at dry-ice temperature for krypton, and at liquid-nitrogen temperature for argon. Aliquots of the gas mixture were introduced to the cryostat through a stainless-steel tube until the light intensity was observed to drop by 30% to 80%.

A major experimental problem which arises in combining vacuum-ultraviolet spectroscopy with cryogenic techniques is the slow condensation of extraneous vapors onto the sample surface, resulting in a general, continuous absorption below 1500 Å. Previous workers have encountered this difficulty and have taken various steps to minimize it.[1–6,12,13] The problem has never yet been really solved. In this experiment lithium fluoride windows were used so that the sample-holder–cryostat system was separated from the rest of the monochromator, eliminating a large source of possible contamination. This, however, limited the experiment to energies lower than 11.8 eV, which corresponds to the onset of strong absorption by lithium fluoride. Secondly, it was found that, if the pumping system was connected to the cryostat at a position furthest from the sample, the large cold surfaces of the cryostat, at 77° and 4°K, acted as very efficient cryopumps eliminating all back flow of diffusion-pump oil. Under these conditions the sample could be maintained at the temperature of the experiment, approximately 20°K, for an hour or more with a decrease in the light intensity of from 2%–5%.

A hydrogen-source spectrum was recorded immediately before the sample was deposited, and again immediately afterwards. The decrease of intensity at every hydrogen-emission line was then measured. The hydrogen spectrum is rich in lines in the region of 1050 to 1600 Å and, under the experimental conditions of relatively high resolution, approximately 40 peaks per 100 Å were available. Decrease in the valleys between emission peaks provided additional points in regions where the absorption was rapidly changing. The average of at least two absorption curves was calculated in each spectrum reported. Due to the slow scanning rate used (10 Å/min) and the short lifetime of a given charge of liquid helium, the entire absorption spectrum of up to

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[9] G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

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[12] M. Cardona and D. Greenway, Phys. Rev. **131**, 98 (1963).

[13] J. Kwak and G. Robinson, J. Chem. Phys. **36**, 3137 (1962).

300 Å could only be measured in several runs, using several separate sample deposits. The curves obtained were pieced together by scaling small overlapping regions after conversion to an optical density (logarithmic) scale.

Measurements were corrected for scattered light and surface reflection. The scattered light was assumed to be constant throughout the wavelength region, and was measured at 900 Å where hydrogen does not emit.

The gas-phase spectrum of acetylene was measured from 2050 to 1050 Å in preliminary experiments. A 10-cm cell with LiF windows was used. The pressures of acetylene were 15, 100, and 323 μ Hg. The monochromator slitwidths were 20 μ, corresponding to a resolution of approximately 0.4 Å. Below 1650 Å the hydrogen source produces a many-lined spectrum. In order to utilize the high resolution of the instrument, the absorption must actually be measured at a number of wavelengths larger than the number of hydrogen emission lines. To facilitate this procedure, a digital data-recording system was used which was designed to record on punched paper tape transmittance and wavelength data generated by the spectrophotometer. After the data from the through beam were recorded on paper tape and the sample had been placed in the path, the recording system provided an analog curve on a strip chart recorder of the ratio of voltages generated by variations of data received from a paper-tape reader and transmittance data of the test sample. The tape reader is designed to be coupled to the encoder on the wavelength shaft to guarantee correct alignment. In this way absorption measurements could be made every 0.06 Å, which takes full advantage of the available instrumental resolution.

III. EXPERIMENTAL RESULTS

A. Acetylene

The Rydberg series of acetylene were first assigned by Price in 1935, using spectra obtained with a 2-m grazing incidence spectrograph.[14] Wilkinson re-examined the relevant spectral region in 1958 with a 21-ft spectrograph, and confirmed Price's assignments.[15] Moe and Duncan[16] have reported the intensities of the Rydberg bands, but the photographic techniques they used are subject to large error and their values are quite different from those obtained by Watanabe[17] and in this work.

The two series observed fit the formulas

$$\nu_0^n = 92\,076 - R/(n-0.50)^2, \qquad (1)$$

$$\nu_0^n = 91\,950 - R/(n-0.95)^2, \qquad n=3,\,4,\,5. \qquad (2)$$

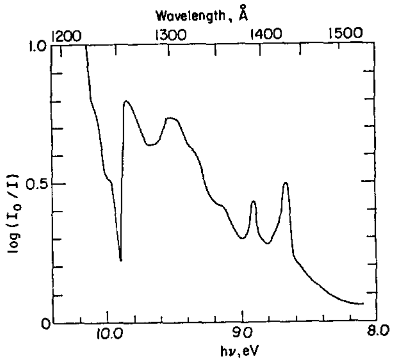

FIG. 1. Absorption spectrum of acetylene-doped (1%) krypton matrix from 1200 to 1520 Å.

From the limits of the Rydberg series the ionization potential is calculated to be 11.35±0.01 eV.

In the bands having low values of n, much vibrational structure is observed. For bands having higher principal quantum numbers, the vibrational structure is obscured by the overlapping of subsequent electronic transitions. The first Rydberg transition of 1520 Å is very strong. This and the next two vibrational components at 1479 and 1440 Å are well separated from the transitions at higher energies. This separation was found to be useful in identifying the bands observed in the solid matrix. These three bands are separated by intervals of 1820 cm^{-1}.

Acetylene is an appropriate molecule to study in the solid state because, due to its low ionization potential—relative to other small molecules—the first Rydberg transition in the gas phase is found at 1520 Å which is in the range of standard sources. Furthermore, it is isoelectronic with N_2, is small, and is stable. Recently, Brith and Schnepp have measured the spectrum of solid N_2 to 1200 Å. But the ionization potential of CO is 14.1 eV and that of N_2 is 15.51 eV. Rydberg series for these small diatomic molecules begin only at wavelengths below 1000 Å in the gas phase.

Figure 1 shows the absorption spectrum of a krypton matrix doped with 1% acetylene. The sharp rise at 1220 Å represents the threshold absorption of the krypton matrix. Two sharp absorption peaks are observed at 1430 and 1392 Å. Above 1430 Å the absorption drops quickly, and the absorption levels off above 1500 Å.

Figure 2 shows the spectrum of an argon matrix doped with 1% acetylene. Two absorption peaks are observed at 1375 and 1344 Å. At higher energies the absorption is continuous with little structure, although a few broad peaks are observed. At wavelengths above 1375 Å the absorption falls quickly and nearly levels off above 1430 Å. Figures 1 and 2 are very similar; the argon spectrum is simply shifted in the direction of higher energy.

The parentage of the observed peaks can be established by comparison with the acetylene gas-phase

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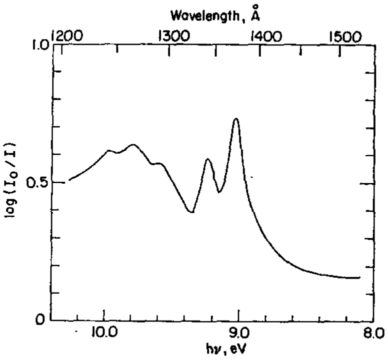

FIG. 2. Absorption spectrum of acetylene-doped (1%) argon matrix from 1200 to 1520 Å.

spectrum. The first Rydberg transition in the gas phase at 1520 Å has an absorption coefficient of around $k=15\,000$ cm^{-1}, the second $k=1500$ cm^{-1}, and the third $k=500$ cm^{-1}. The spacing between the peaks is 1820 cm^{-1}. The absorption above 1520 Å drops off sharply and from 1540 to 2000 Å the absorption coefficient is approximately $k=10$–50 cm^{-1}. Toward higher energies, beyond the first three Rydberg vibronic bands, the transitions are very close together and apparently superimposed on a continuum.

The first two peaks observed in each of the solid spectra are therefore undoubtedly the 1520- and 1479-Å bands of the gas-phase spectrum. The spacing between these two peaks in Fig. 1 is 1960 cm^{-1} as compared with 1820 cm^{-1} in the gas spectrum, reflecting a vibrational perturbation induced by the matrix. McCarty and Robinson[2] have measured the spectrum of C_2 in solid xenon and found the symmetric C–C stretching frequency in the ground state of C_2 to be increased from 1618 cm^{-1} in the gas phase to 1720 cm^{-1} in the xenon matrix. The same vibrational frequency in an excited electronic state was increased from 1755 to 1940 cm^{-1}.

The remaining Rydberg states, which are resolved in the gas spectrum, seem to be broadened seriously and are not resolved in either matrix spectrum.

The first acetylene Rydberg band is shifted from 8.155 eV in the gas phase to 8.67 eV in krypton and to 9.01 eV in argon. Attempts to trap acetylene in a neon matrix were not successful. In a xenon matrix no absorption bands were observed at wavelengths higher than the xenon threshold of absorption at 1500 Å. This sets one limit on the acetylene Rydberg shift in xenon as greater than 0.17 eV.

The magnitudes of the acetylene shifts are very similar to those of the xenon $^3P_1$ state. The gas-phase excitation energy of xenon, 8.43 eV, is close to the acetylene value 8.155 eV. The $^3P_1$ state of xenon is shifted to higher energies by 0.58 eV in krypton and 0.79 eV in argon.

B. Benzene

In studying matrix effects on molecular Rydberg states it is helpful if the Rydberg system is made up of strong and well-separated lines. The bands observed in the spectrum of the solid are then readily identified. Benzene has such a sharply defined Rydberg spectrum. Price and Wood first observed the far-ultraviolet spectrum of benzene and arranged the discrete bands into the Rydberg series which converged to approximately the same limit, corresponding to an ionization potential of 9.24 eV.[18] Wilkinson repeated the experiment using a 21-ft spectrograph and observed two additional series of weaker intensity.[19] The two strong series fit the formulas

$$\nu_0^n = 74\,587 - R/(n+0.84)^2, \qquad (3)$$

$$\nu_0^n = 74\,587 - R/(n+0.54)^2, \qquad n=2,\,3,\,4,\,\cdots. \qquad (4)$$

Table I gives the positions of the lines of the two strong series. The vibrational components of each electronic transition are extremely weak and are not listed in Table I. Price and Wood ascribed this weakness to the nonbonding nature of the excited electron.

Figure 3 shows the absorption spectrum of a benzene-doped krypton matrix from 1300 to 1600 Å. Below 1600 Å the absorption increases rapidly, and at 1543 Å it drops suddenly to give the first of a series of sharp negative peaks corresponding to decreases in absorption. Figure 4 shows the absorption spectrum of a benzene-doped argon matrix from 1300 to 1600 Å. It is similar to Fig. 3 and shows the same anomalous structure but at different energies. The first several negative peaks are very sharp and well separated. Those at higher energies seem to be partially overlapping and are not as well defined. Table II lists the energies at the minima of the negative peaks.

IV. DISCUSSION

In the past two years, our understanding of impurity states in rare-gas solids has undergone a major change. In order to find a suitable approach to the theoretical treatment of Rydberg states in the solid state, it is useful to review briefly some recent developments.

The first serious calculations on excited states in rare-gas crystals were performed by Knox in 1959.[20]

TABLE I. Benzene Rydberg energy levels—observed values.[a]

	Series I		Series II	
n	(eV)	(Å)	(eV)	(Å)
3	8.145	1522	8.37	1481
4	8.59	1444	8.68	1428
5	8.80	1408	8.85	1400
6	8.93	1388	8.95	1384
7	9.01	1376	9.92	1374

[a] See Ref. 18.

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[18] W. Price and R. Wood, J. Chem. Phys. **3**, 439 (1935).

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He presented a formalism based on Frenkel's theory of excitons[21] from which excitation energies, band structure, effective masses, and integrated absorption cross sections could be calculated. He then proceeded to apply the formalism to the case of crystalline argon. The justification given for applying the Frenkel–Peierls theory to rare-gas solids was that these solids consist of cubic lattices of tightly bound closed shells in the ground electronic state, and have large lattice constants. The Frenkel–Peierls formalism led to a calculated red shift of 2 eV, whereas the experimental spectrum showed a shift of 0.5 eV to the blue.[8] Gold[22] used a similar approach to predict a 4-eV blue shift of the argon $^1S_0$–$^3P_1$ transition in a neon matrix, whereas the experimentally observed blue shift is 0.5 eV.

The experiments of Baldini which showed these calculated matrix shifts to be in serious error simultaneously revealed the existence of additional absorption lines which could not be meaningfully explained in terms of the Frenkel model.[8,9] The lines could be explained in terms of Wannier excitons, since their energies fit a hydrogenic formula as modified for effective-mass impurity states[23]:

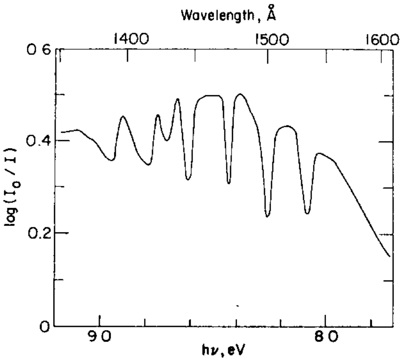

FIG. 3. Absorption spectrum of benzene-doped (1%) krypton matrix from 1300 to 1600 Å.

$$E_n=(m_e^*e^4/2\hbar\epsilon^2)(1/n^2), \qquad (5)$$

where m_e^* is the effective electron mass and ϵ the dielectric constant. This failure of the Frenkel model in rare-gas solids, in spite of the tightly bound closed-shell ground states and large lattice parameters, led to the general agreement that excitons in rare-gas solids were of an intermediate radius, and that the Frenkel and Wannier models were complementary.

If the exciton radius is intermediate in magnitude, the reason for the inadequacy of the Heitler–London scheme is its failure to take into account any charge delocalization in the excited crystal. One way of introducing this charge delocalization into the calculations is to mix charge-transfer states into the crystal wavefunction. Webber *et al.*[24] calculated the first transition of crystalline neon and found that charge delocalization did indeed decrease the energy of the exciton orbital. Webber *et al.* also calculated the energy of the first electronic excitation of an argon atom in a neon matrix, the same problem Gold had studied. By including extensive charge delocalization the predicted transition energy was found to be 13.1 eV, compared with the experimental value of 12.7 eV. This represents a substantial improvement over the earlier calculation. Examining the possibility of representing charge delocalization without charge-transfer states, Webber *et al.* also tried a pseudopotential formalism[25–27] together with a model Hamiltonian of a dielectrically screened hydrogenic type.

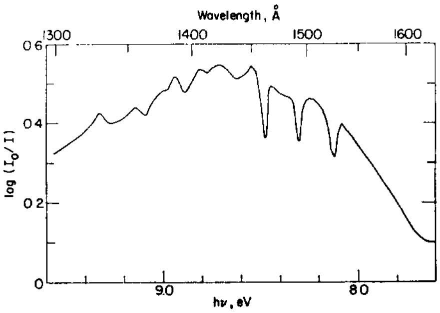

FIG. 4. Absorption spectrum of benzene-doped (1%) argon matrix from 1300 to 1600 Å.

The supermolecule formalism is essentially a Frenkel scheme with large charge delocalization introduced by adding charge-transfer states. The pseudopotential formalism with a dielectrically screened hydrogen model Hamiltonian is, similarly, a modification of the Wannier scheme. Thus, the result of Webber's work is to offer two more reasonable alternatives than the Frenkel and Wannier schemes provided.

TABLE II. Transmission increases observed in benzene-doped matrices.

Argon		Krypton	
(Å)	E (eV)	(Å)	E (eV)
1527	8.12 (S)[a]	1534	8.08 (S)
1494	8.30 (S)	1501	8.26 (S)
1462	8.48 (S)	1470	8.43 (S)
1438	8.62 (D)	1441	8.60 (D)
1412	8.78 (D)	1424	8.70 (D)
1394	8.89 (D)	1413	8.77 (D)
1363	9.09 (D)	1384	8.96 (D)

[a] S, sharp; D, diffuse.

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[21] J. Frenkel, Phys. Rev. **37,** 17, 1276 (1931).

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[26] M. Cohen and V. Heine, Phys. Rev. **122,** 1821 (1961).

[27] B. Austin, V. Heine, and L. Sham, Phys. Rev. **127,** 276 (1962).

The criteria for determining which of the alternatives is more useful in a given case are now fairly specific.[24] In cases where the conduction band of the solid matrix is free-electron-like, the excited hydrogenic orbital is much larger than the localized wavefunction, and a dielectrically screened hydrogenic Hamiltonian will provide an accurate description of the crystal states. If the conduction band is not free-electron-like, the Wanner function is spread out over many unit cells so that the central cell correction becomes large, and it is then necessary to use the supermolecule formalism.

The problem of treating intermediate excitons, such as molecular Rydberg states in rare-gas solids, would seem best approached through the use of the model Hamiltonian technique because of the free-electron-like nature of the matrix. Although a simple dielectrically screened hydrogenic Hamiltonian may not be adequate, the pseudopotential formalism will undoubtedly prove useful.

Comparing Table II with the gas-phase Rydberg levels of Table I reveals a similarity in the location of the transmission increases and the Rydberg levels, but not a one-to-one correspondence. The striking features clearly represent some interaction between the benzene molecular states, most likely the Rydberg states, and some matrix states, most likely the continuum states of the conduction band. Configuration interaction between discrete atomic states and atomic continuum states has been observed previously to give anomalous line shapes, either strongly asymmetric absorption peaks or transmission windows of the type observed here. Fano is responsible for the development of the theory describing such anomalous line shapes as were first observed in optical spectra associated with autoionization in simple atomic systems.[28]

It is configuration interaction between the continuum of states which exists at energies higher than the first atomic ionization potential, and a configuration in which two electrons are excited, that gives rise to autoionization, since the wavefunction of the quasidiscrete level becomes coupled with those of the neighboring levels of the continuum.[29] Predissociation is the analogous phenomenon in molecules, whereby a molecule may spontaneously dissociate if it is put into a quasidiscrete state in which its energy exceeds the energy necessary for dissociation. This problem was treated first by O. K. Rice in 1933.[30]

The first observation of anomalous line shapes in absorption experiments was made in rare-gas spectra in the region between the two ionization thresholds corresponding to the doublet ${}^2P_{\frac{3}{2},\frac{1}{2}}$ ground states of rare-gas ions.[31] The atomic Rydberg levels converging to the ${}^2P_{\frac{1}{2}}$ limit lie at energies higher than the ${}^2P_{\frac{3}{2}}$ limit, and the absorption peaks between the two limits are strongly asymmetric. Fano treated this particular problem in an early theoretical paper.[32]

Autoionization in He is of interest since a transition to discrete levels above the first ionization limit requires that both electrons be excited. Transitions to autoionizing energy levels in helium have been observed near 60 eV. The line shapes are strongly asymmetric, absorption being enhanced on the low-energy side and reduced on the high-energy side.[33]

Autoionization can result from the excitation of inner-shell electrons as well as from double-electron excitations. Samson[34] has observed autoionized energy levels in argon and krypton at around 25–30 eV, which showed a decrease in absorption with no accompanying increase.

The optical absorption spectra of metal vapors, corresponding to the excitation of an inner electron from a closed subshell, provide examples of several possible types of line shapes. Calcium shows discrete peaks of normal symmetric shape which are much stronger than the accompanying continuum.[35] Thallium vapor shows a highly asymmetric peak near 2000 Å, with a dip in the ionization continuum followed by a sharp peak.[36] Lead vapor near 1672 Å shows a sharp minimum in the ionization continuum without a corresponding peak.[37]

Fano-type line shapes are therefore not unusual in atomic spectra. In fact, the Rydberg series associated with inner-electron or multiple-electron excitations become the dominant features of atomic spectra in the far-ultraviolet absorption region. Two recent reviews have summarized the experimental data in this field.[38] Similarly, spontaneous ionization may occur in molecules, and the spectrum of N_2 near 700 Å shows sharp minima in the ionization continuum associated with such preionization.[39]

The mechanism whereby configuration interaction of the kind just discussed arises may be either inner-shell-electron or two-electron excitations, but is not limited to these. In the case of the solid-benzene-matrix system continuum states can be provided by the conduction band of the matrix. Phillips[40] has discussed the fundamental optical spectra of a large number of solids with respect to line shapes and configuration interac-

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[37] W. R. S. Garton, J. Quant. Spectry. Radiative Transfer **2,** 335 (1962).

[38] U. Fano and J. W. Cooper, Phys. Rev. **137,** A1364 (1965); R. E. Huffman, Physical Sciences Research Papers No. 66 (U.S. Department of Commerce, Office of Technical Services, Washington 25, D.C.).

[39] R. E. Huffman, Y. Tanaka, and J. C. Larrabee, J. Chem. Phys. **39,** 910 (1963).

[40] J. C. Phillips, "Fundamental Optical Spectra of Solids," (to be published).

tion of exciton resonances, and Jain[41] has considered in detail the spectrum of solid xenon. From their work we can make the following comments.

The optical spectra of solids include features arising from both interband and intraband transitions. Direct interband transitions are associated with the production of free-electron–hole pairs and are characterized in the spectra by absorption edges. In addition to the first absorption threshold there may be absorption edges at higher energies corresponding to transitions taking place at other points of the Brillouin zone.

Intraband transitions are associated with exciton states which arise as a result of electron–hole attraction. In this approach it is the Wannier exciton model which is generally valid, since the Wannier exciton is constructed from an electron wave packet made up of states from the conduction band and a hole wave packet of states from the valence band. Below the direct absorption threshold a Rydberg series of hydrogenic excitons is formed representing bound states.[42]

Exciton resonances may also occur above the direct threshold absorption and are associated with the higher energy interband structure. Because these excitons lie above the direct interband threshold and configuration interaction with scattering states is possible, they do not represent stable bound states.

Jain, in analyzing the solid xenon spectrum, noted that stable bound excitons below the direct absorption threshold are characterized by narrow resonances separated by broad antiresonant minima, whereas metastable excitons show broad resonant peaks and sharp narrow antiresonances.[41]

From the convergence limit of the hydrogenic bound exciton states observed in rare-gas solids, we can obtain a value for the energy gap E_G between the valence and conduction bands, since

$$(h\nu)_n = E_G - (G/n^2), \qquad n=1, 2, 3, \cdots,$$
$$G = \mu\epsilon^{-2}\ \text{Ry}, \tag{6}$$

where μ is the reduced mass of the exciton, and Ry is the Rydberg constant, 13.6 eV. From the data of Baldini[43] on solid rare-gas alloys we find $E_G = 9.28$ eV for xenon, 11.67 eV for krypton, and ~14 eV for argon.

When a xenon atom is placed in an argon matrix the hydrogenic lines of xenon are still observed but the series converges to the conduction band of the matrix.[44] Continuum states are reached by transitions at much lower energies in the solid than in the gas. For example, the ionization potential of gaseous xenon is 12.08 eV whereas transitions to continuum states in the solid, whether the pure xenon solid or some other matrix, occur at 9–10 eV.

The spectra displayed in Figs. 3 and 4 can be readily explained in terms of transitions to discrete molecular states which overlap the conduction-band states of the matrix. The sharp antiresonance in Fig. 1 at 9.9 eV might similarly represent one of the higher-series members of acetylene interacting with krypton conduction-band states, which would imply that the energy gap between the impurity level and the matrix conduction is between 9.0 and 9.9 eV.

A complete analysis of the line shapes in Figs. 3 and 4 is made difficult by the overlapping of neighboring antiresonances. In particular, one cannot evaluate Fano's parameter q^2, which represents the relative transition probabilities to the discrete state, as modified by continuum states, and to the bandwidth of unperturbed continuum states. One can only say that, since nearly pure transmission windows are observed, with little or no increased absorption, q is much smaller than unity. Since transitions to the discrete states in the gas phase have absorption coefficients as high as 10^3 cm^{-1}, this result implies that the discrete states are greatly modified in the solid. Values of the bandwidth Γ vary from about 0.03 to 0.05 eV, corresponding to a decay rate of $\sim 6\times 10^{13}$ sec^{-1} for the metastable state. Since Γ is related to that interaction element V of the energy matrix connecting the discrete state ϕ, with appropriate continuum states ψ_i, we have

$$V = \langle \psi_i \mid H \mid \phi \rangle = (\Gamma/\pi)^{\frac{1}{2}} = 0.11\ \text{eV}. \tag{7}$$

The spectrum of pure solid benzene, and pure solid acetylene, showed only strong broad continuous absorption in the region from 1600 to 1300 Å. It seems, therefore, that a proper, i.e., free-electron-like, conduction band is required for the appearance of molecular antiresonances. This fact prevents the exact location of the photoconducting level in solids whose band structure is more complicated than that of rare gases. One can say, in the case of benzene in a rare-gas solid, merely that the level is below 8.0 eV, which is certainly a reasonable limit. Photoconductivity experiments in benzene-doped matrices would confirm the conclusions of this work, and experiments on solid benzene would locate the band gap where the optical method fails.

In conclusion, it is in order to discuss the relevance of this experiment to the problem of describing molecular crystal excitations in general. It is commonly assumed that the Frenkel model of molecular excitations is a useful formalism to describe the lower excited states of crystals of aromatic molecules. The justification given is that the spectrum of the molecular solid is similar to that of the gas with regard to transition energies. This similarity is offered as evidence that the molecular wavefunctions are only slightly perturbed from those of the isolated molecule.

Even in the case of solid rare gases, early workers used an unmodified Frenkel scheme, with the justification that the ground states of the atoms were tightly bound closed shells and only van der Waals forces

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stabilized the crystal.[18] Also, from Baldini's studies we know that the ${}^1S_0$–${}^3P_1$ transition energy in xenon changes only slightly in going from the gas to the solid. This was also used as evidence that the Frenkel scheme was appropriate for rare-gas solids.[20] In retrospect it is clear that the Frenkel model is not valid for solid rare gases. The argument concerning the tightly bound ground state is irrelevant to the location of the first crystalline excited state, and the small shift in going from the gas to the solid can be shown merely to reflect the delicate balance between large Coulomb and exchange effects.[24] It is now clear that the rare-gas ${}^1S_0$–${}^3P_1$ transition should be treated either by a Frenkel scheme modified by the inclusion of large charge delocalization, or in terms of the first member of a Wannier hydrogenic series. In fact, the remaining features of the rare-gas crystal spectra can be treated only within the Wannier framework.

Finally, even in cases where the Frenkel scheme would seem to be most applicable, such as the low-energy excitation of crystalline naphthalene, charge delocalization must be introduced—via mixing of charge-transfer states—in order to calculate the correct Davydov splitting.[45] But inasmuch as charge-transfer states have not yet been observed directly in aromatic crystals,[46] the results of the present experiment constitute the only unambiguous evidence that aromatic crystals cannot be described solely in terms of slightly perturbed free-molecule wavefunctions.

ACKNOWLEDGMENTS

We wish to thank the U.S. Public Health Service and the Directorate of Chemical Sciences of the Air Force Office of Scientific Research for financial support. We have also benefited from the use of facilities provided by ARPA for materials research at the University of Chicago. Finally, we wish to thank Professor J. C. Phillips for several helpful discussions.

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 9 1 NOVEMBER 1965

Eigenparameters for the $1s\sigma_g$ and $2p\sigma_u$ Orbitals of H_2^+ *

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(Received 7 June 1965)

Eigenparameters for the $1s\sigma_g$ and $2p\sigma_u$ electronic orbitals of the hydrogen molecule ion are investigated. The appropriate parameters are tabulated for the internuclear separations $R=1.0(0.5)30.0\ a_0$, and more extensive tabulations, available elsewhere, are described.

THE hydrogen molecule ion (H_2^+) is of considerable practical and theoretical interest. Knowledge of the higher vibrational states of the electronic ground state is required for study of various dissociation mechanisms,[1,2] and the potential curves for higher electronic states are needed,[3] if processes involving electronic transition are of interest. Also, energy differences between the $1s\sigma_g$ and $2p\sigma_u$ states are required, especially at large R, for the treatment of charge transfer[4–6] between the proton and hydrogen atom. Many problems concerned with molecular structure, such as the evaluation of various matrix elements[7] and the treatment of scattering phenomena,[3,4] require the eigenfunctions as well.

The useful tabulation by Bates, Ledsham, and Stewart[8] provides the necessary eigenparameters for a number of states over the range of internuclear separations

$$R=0.0(0.2)5.0(0.5)10.0a_0.$$

Wallis and Hulburt[9] tabulate the eigenparameters for several states, but they only consider a few widely spaced values of R. A recent paper by Wind[10] gives the electron energy for the ground state with detail

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* This work was supported by the U.S. Atomic Energy Commission.

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