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Intravalence and Extravalence Excitations of the Ethylene Molecule in Liquid and Solid Rare Gas Matrices

Eli Miron, Baruch Raz, and Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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In this paper we present the results of a spectroscopic study of the absorption spectra of ethylene and ethylene-d_4 in liquid argon, liquid krypton, and solid krypton in the spectral region 2000–1400 Å. The samples involved 1 cm thick doped liquids and 1 cm thick doped krypton crystal (doping level 1–10 ppm). The intravalence nature of the $N\rightarrow V$ transition was confirmed. On the basis of some general criteria based on vibrational structure, vibrational isotope effects, matrix shifts, and line broadening we were able to provide a definite identification of the lowest Rydberg state of ethylene and of ethylene-d_4 in solid krypton. The effect of the liquid–solid phase transition on the line broadening in the lowest Rydberg state was elucidated. We were also able to provide the first experimental observation of the $n=2$ impurity Wannier state originating from the molecular positive ion in liquid argon.

I. INTRODUCTION

Recent experimental studies of the excited electronic states of rare gas alloys resulted in the identification of Wannier type atomic impurity states in solid rare gases.[1–3] In particular, it was demonstrated that the rare gas "atomic" doublets ${}^1S_0\rightarrow{}^3P_1$, ${}^1P_1$ are quite closely located to the position expected for a $n=1$ Wannier state, while a new series of absorption bands, which have no parentage in the excited states of the isolated constituents, correspond to a hydrogenic manifold of higher Wannier levels converging to the bottom of the conduction band of the matrix.[4] Extravalence excitations of polyatomic molecules trapped in solid rare gases are expected to exhibit similar behavior. Recent experimental work has unambiguously established that the lowest molecular Rydberg states of benzene, acetylene, ethylene-d_4, carbon disulfide, and sulfur dioxide are amenable to experimental observation in rare gas solids.[5–7]. These observations concur with theoretical arguments which indicate that rare gas solids constitute an ideal medium for the observation of molecular Rydberg states in solids in view of the weak electron–atom interaction so that line broadening is not excessive.[8] Furthermore, the free electronlike nature of the conduction band[9,10] leads to a normal hydrogenic Wannier series. In this context, it should be noted that the lowest molecular Rydberg states in a simple rare gas solid correspond to an intermediate situation which can be either described in terms of the tight binding approximation considerably modified by overlap orthogonality corrections, or by the $n=1$ Wannier state with appreciable central cell corrections. Neither of these theoretical schemes is perfect, and the choice is just a matter of convenience. Semiquantitative theoretical arguments and experimental data demonstrate that the lowest molecular Rydberg state in a rare gas solid is blue shifted by 0.5–0.8 eV relative to the corresponding extravelence excitation in the gas phase.[11] While the lowest Rydberg state in a matrix can be qualitatively related to a strongly perturbed excitation of the "isolated" molecule, the higher excited molecular impurity levels in the matrix will not bear any relation to the molecular excitations in the gas phase. Experimental evidence for the $n=2$ Wannier state of a molecular impurity in rare gas solids was recorded for the case of the benzene molecule.[12]

The theoretical treatment of Wannier type molecular impurity states in rare gas solids rests on the translational symmetry of the host lattice. Recent experimental work has demonstrated that symmetry restrictions can be relaxed in this context and that Wannier impurity states are amenable to experimental observation in liquid rare gases.[13,14] These studies focused attention on Xe atomic impurity states in liquid Ar and Kr. It will be of considerable interest to extend previous work and to study extravalence molecular excitations in a simple disordered system, such as liquid rare gases.

In the present work we present the results of vacuum ultraviolet spectroscopic work on ethylene and ethylene-d_4 in some liquid and solid rare gases. The implications and applications of the study of the excited electronic states of this molecular impurity in a dense medium are:

(a) The lowest Rydberg state of the ethylene molecule overlaps the intravalence $N\rightarrow V$ transition in the gas phase. In a simple dense medium the V state is expected to behave quite differently from the Rydberg state. Spectroscopic studies in such a medium should prove useful to distinguish between extravalence and intravalence excitations.

(b) The nature of the $N\rightarrow V$ transition of ethylene is still controversial.[15–18] Preliminary results on the $\pi\rightarrow\pi^*$ transition of ethylene in liquid and solid rare gases have established the intravalence nature of this transition,[19] and further evidence concerning this point will be reported in the present work.

(c) The effects of "symmetry breaking" on the higher excited states of a molecular impurity upon

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melting of the matrix are of considerable interest. In particular, it is interesting to establish under what conditions Wannier impurity states (originating from a positive molecule hole) can be experimentally observed in a liquid rare gas.

(d) The ethylene molecule, which is characterized by the first gas phase ionization potential of 10.5 eV,[20] can be used as a probe for the spectroscopic study of one photon ionization processes in solid and liquid dense media.

II. THE IDENTIFICATION OF ETHYLENE IMPURITY WANNIER STATES IN SOLID AND LIQUID RARE GASES

The identification of the Wannier states of ethylene in rare gas matrices is complicated due to the overlap of these extravalence excitations with the intravalence $N \rightarrow V$ transition.[21] The following guidelines, based on previous work on atomic impurity states in solid and liquid rare gases[14] and on molecular impurity states in solid rare gas matrices,[5] should be applied for the problem at hand:

a. Vibrational structure. The $N \rightarrow R$ transition of the ethylene molecule in the gas phase exhibits a doublet structure revealing the totally symmetric ν_2 progression simultaneously with an even change of the twisting ν_4 mode. The relevant vibrational frequencies are $\nu_2 = 1370$ cm^{-1} and $2\nu_4 = 472$ cm^{-1} for C_2H_4 and $\nu_2 = 1295$ cm^{-1} and $2\nu_4 = 282$ cm^{-1} for C_2D_4.[21] The lowest Rydberg state of both ethylene and of deuteroethylene in solid and liquid matrices should exhibit the totally symmetric ν_2 vibration, but the $2\nu_4$ spacing may not be observable due to line broadening. Similar vibrational structure is expected to be exhibited by higher $n=2$ Wannier states of the ethylene impurity, as the positive molecular ion is not expected to be appreciably perturbed by the matrix.

b. Isotope effects. While the vibrational structure for the $N \rightarrow R$ transition of ethylene is not appreciably affected by deuterium substitution, the situation is drastically different for the $N \rightarrow V$ transition in the "free" ethylene and ethylene-d_4 molecules. The $\pi \rightarrow \pi^*$ transition of ethylene-h_4 exhibits well resolved broad bands, each consisting of a large number of overlapping, transitions characterized by the same value of $v_2 + v_4$. whereas the vibrational frequencies ν_2 and ν_4 are close. The $\pi \rightarrow \pi^*$ spectrum is radically different in C_2D_4 as the ν_4 frequency considerably diminishes upon dueteration resulting in a complex gas phase spectrum which is not resolved under experimental medium resolution conditions as employed in the present work. On the other hand, the gross features of the lowest $N \rightarrow R$ are not drastically affected under deuteration. Thus a comparative study of C_2H_4 and C_2D_4 in dense media is expected to provide us with an important tool for the distinction between intravalence and extravalence excitation.

c. Spectral shifts. The lowest molecular Rydberg state (or the $n=1$ Wannier state) of a molecular impurity in rare gas liquid or solid is expected to exhibit an appreciable blue spectral shift relative to the gas phase value.[11] For a series of different solid or liquid matrices these blue matrix gas spectral shifts are in the order $Xe < Kr < Ar$, while the blue shift is appreciably larger in the solid than in the corresponding liquid (see Table I). On the other hand, intravalence $\pi \rightarrow \pi^*$ excitations should exhibit a mild red shift relative to the gas phase spectrum.[22] This red shift is expected to increase with increasing the polarizability of the medium atoms, and should be only slightly affected by passing from the liquid to the corresponding solid.

d. Nature of Wannier molecular impurity states. Higher Wannier impurity states (characterized by the principle quantum number $n > 2$) bear no relation to the higher Rydberg extravalence state of the isolated molecule. These energies, E_n, of the Wannier states are described in terms of a hydrogenic maifold

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

where $G = 13.6(m^*/k^2)$ eV, m^* corresponds to the effective mass in the solid or the liquid ($m^* \sim 0.5m$ for solid and liquid Ar and Kr)[23], while k is the static dielectric constant. E_G represents the molecular impurity band gap (see Sec. II.e). It should be noted that E. (1) represents the electronic origin of each transition. These higher Wannier states retain only a single feature bearing to the properties of the isolated molecule, as they are expected to reveal a vibrational progression exhibiting the stretching vibrational frequency ν_2 (and possibly also other vibrational modes) of the high Rydberg states (which are close to those of the positive ion). Thus each of the molecular Wannier impurity states of ethylene and of ethylene-d_4 are expected to be distributed in terms of a progression

$$E_{n.V} = E_n + v\hbar\nu_2. \tag{1'}$$

TABLE I. The matrix effect on the transition energies of intermediate excitons.

Guest/host	Gas (Å)	Ar(l) (Å)	Kr(l) (Å)	Kr(s) (Å)
$Xe(^3P_1)$	1470	1420	1450	1410
$Xe(^1P_1)$	1296	1230	1265	...[b]
C_2H_4 [a]	1742	1640[c]	1680[c]	1606
C_2D_4	1737	1631[c]	1664[c]	1635

[a] First vibrational band of the Rydberg transition (mean value over the doublet).

[b] Obscured by krypton peak.

[c] Maximum of observed, unresolved, absorption peak.

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This is a distinct feature of molecular Wannier impurity states.

e. Ionization limit in a dense medium. The impurity band gap E_G [Eq. (1)] corresponds to the ionization in a dense (solid or liquid) medium. The electronic origin of the transition to the bottom of the conduction band can be related to the gas phase ionization potential, I_g, the polarization energy, P_+, of the positive hole, and the energy V_0 of the bottom of the conduction band via[4,14]

$$E_G = I_g + P_+ + V_0. \qquad (2)$$

The ionization process of a molecule in a dense medium may produce the positive ion core in different vibrational excited states. The most pronounced vibrational frequency is expected to be the stretching mode ν_2. We thus expect that the ionization limit of a molecular impurity will not just follow the density of states in the conduction band (as is the case of an atomic impurity) but will rather exhibit a vibrational structure, which in the simplest case will be given by

$$E_{G,V} = E_G + v\hbar\nu_2. \qquad (2')$$

f. Line broadening. Line broadening of large radius impurity states can be theoretically handled within the framework of the weak scattering limit resulting in the line width

$$\Delta\nu = \frac{\rho_0 \hbar^2 \tilde{a}^2 S(k) k}{m^*} \cong \frac{\hbar^2 k}{m^*}\left(\frac{m^*}{\pi k_B T}\right)^{1/2}\left(\frac{2}{\mu m^*}\right)\frac{S(k)}{S(0)}, \qquad (3)$$

where ρ_0 is the number density of the liquid, $\tilde{a}$ the scattering length in the liquid, $s(k)$ corresponds to the structure factor of the dense fluid, while in the limit $k \rightarrow 0$, $S(0) \cong \chi k_B T$, where χ is the isothermal compressibility and μ is the low field electron mobility. From this theoretical result we can conclude that: (f1) the linewidth in a given (solid or liquid) matrix decreases with increasing n. Although Eq. (3) is not applicable for the $n=1$ lowest Rydberg state we can assess on the basis of this theoretical and of experimental evidence that $\Delta\nu_{n=1} \cong 2\Delta\nu_{n=2}$; (f2) on the basis of the available electron mobility data the linewidth (for a given n) for different matrices should increase in the order Xe<Kr<Ar; (f3) the linewidth for a given n value should be higher in the liquid than in the solid, the ratio being roughly given by $\Delta\nu(\text{liquid})/\Delta\nu(\text{solid}) \simeq \mu(\text{solid})/\mu(\text{liquid})$. From the available electron mobility data we expect appreciable line broadening in the liquid relative to the solid so that $\Delta\nu_n(\text{liquid})/\Delta\nu_n(\text{solid}) \sim 2\text{–}3$ for Ar, Kr, and Xe.[9,10]

III. EXPERIMENTAL

(*a*) *Spectrograph.* The absorption spectra of ethylene in liquid argon and in liquid and solid krypton were monitored photoelectrically in the range 1900–1200 Å using a McPherson 0.3 m Czerny–Turner vacuum spectrograph equipped with a (MgF_2 coated) grating of 2400 lines/mm. The slitwidth was 150 μ resulting in a spectral resolution of 2 Å.

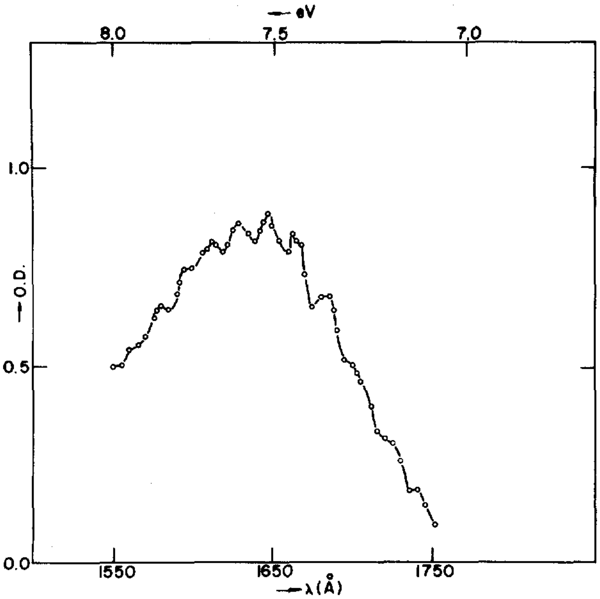

FIG. 1. Absorption spectrum of C_2H_4 in liquid argon (resolution 2 Å).

(*b*) *Light sources.* Tanaka type Xe, Kr, and Ar light sources were employed. Our version of these lamps which provide a good continuous background has been described elsewhere.[24]

(*c*) *Cells.* Optical cells of 1 cm path length sealed with 2 mm thick lithium fluoride windows were used for sample preparation and for the optical measurements. These cells were constructed as previously described[24] to sustain a pressure of 8 atm at 90°K. The cells were attached to a liquid nitrogen dewar, and temperature control (within ±1°K) in the region 65–104°K was achieved by a thermal heater.

(*d*) *Materials.* Matheson research grade rare gases were used. The impurity content of the Ar gas did not exceed 0.1 ppm, while the major impurity content of the Kr gas involved 10 ppm of Xe. The 1 cm thick liquid and solid "pure" matrices did not exhibit any parasitic absorption in the spectral region 1900–1200 Å for the solid Ar and for the liquid Ar matrices, and in the spectral region 1900–1500 A for the solid Kr and for the liquid Kr matrices. Below 1500 A the krypton matrices exhibited the well known absorption of the Xe impurity in the regions 1500–1400 Å and below 1300 Å. Ethylene produced by Phillips Petroleum and ethylene-d_4 from Merck, Sharp and Dohme were used.

(*e*) *Sample preparation.* Argon or kyrpton gases doped with 0.5–5 ppm ethylene or ethylene-d_4 were liquified in the 1 cm optical cell at relatively high pressure of 4–5 atm at the temperature range 105–110°K for liquid Ar

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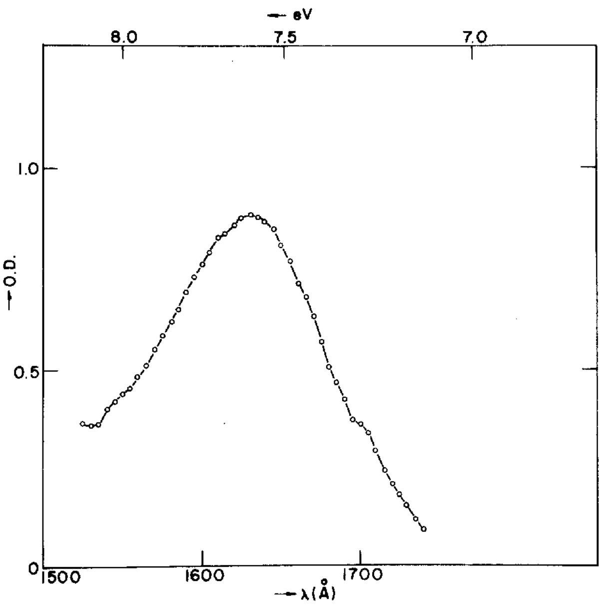

FIG. 2. Absorption spectrum of C_2D_4 in liquid argon (resolution 2 Å).

and 130–135°K for liquid Kr. By monitoring the $\pi\rightarrow\pi^*$ transition of ethylene, it was found that the solubility was adequate both in liquid Ar and in liquid Kr. Thick (1 cm) solid rare gas samples were prepared by moderately slow cooling (0.5°K/min) of the doped liquids under pressure. Again by monitoring of the $\pi\rightarrow\pi^*$ transition it was found that this method is adequate for preparing thick Kr crystals doped with ethylene. On the other hand, ethylene did not dissolve in solid Ar, and the solid sample resulting from slow cooling of C_2H_4/Ar liquid samples was found to be optically transparent over the whole spectral region.

Care had to be exerted not to contaminate the samples within the course of handling. The pressure in the optical cell before the introduction of the gaseous mixtures was lower than 10^{-6} torr. The purity of the gas handling system was checked by liquifying and spectroscopically monitoring pure Ar in the optical cell.

(*f*) *Limitations of the experimental method*: We were able to study the following 1 cm thick samples of liquid and solid rare gases doped with ethylene and with ethylene-d_4: (1) C_2H_4/Ar (l) and C_2D_4/Ar(l) over the region 1900–1200 Å; (2) C_2H_4/Kr(l) and C_2D_4/Kr(l) over the region 1900–1500 Å; (3) C_2H_4/Kr(s) and C_2D_4Kr(s) over the region 1900–1500 Å.

IV. EXPERIMENTAL RESULTS

A. The $N\rightarrow V$ Transition

The absorption spectra of ethylene and ethylene-d_4 in liquid Ar, liquid Kr, and solid Kr in the spectral region 1900–1500 Å are presented in Figs. 1–5. The following points should be noted:

(a) The spectra of C_2H_4 in liquid Ar and in liquid Kr (Figs. 1 and 3) exhibit a long vibrational progession with a mean spacing of 600±100 cm^{-1} (see Table II). The low energy bands (1900–1650 Å) are very similar to the $\pi\rightarrow\pi^*$ transition of the isolated molecule. On the other hand, the high energy bands of C_2H_4 in the liquids ($\lambda<1650$ Å) can be due to the higher members of the $N\rightarrow V$ transition or, alternatively, they may be assigned to the lowest Rydberg state in the liquid matrix.

(b) To resolve this cardinal point concerning the assignment of the C_2H_4 bands in Ar(l) and in Kr(l) at $\lambda<1650$ Å we focus attention on the striking difference between the spectra of C_2H_4 (Figs. 1, 3) and of C_2D_4 (Figs. 2, 4). Under our experimental conditions (spectral resolution of 2 Å) C_2D_4 in liquid rare gases yields a broad unresolved spectrum. On the basis of the gas phase data for the $N\rightarrow V$ transition we expect that for this intravalence excitation the ~600 cm^{-1} vibrational spacing should be resolved for the C_2H_4 molecule and will not be resolved in the C_2D_4 molecule. Thus all the vibrational bands observed for C_2H_4/Ar(l), and for C_2H_4/Kr(l) are assigned to the $\pi\rightarrow\pi^*$ transition, rather than to a Rydberg state.

(c) The spectra of C_2H_4 in liquid and solid Kr (see Fig. 3 and Table I) in the region 1900–1750 Å reveal only a very slight change upon passing from the liquid to the corresponding solid. This is a characteristic feature of an intravalence excitation. Thus all the higher vibrational bands of C_2H_4 in liquid Kr (see Fig. 3)

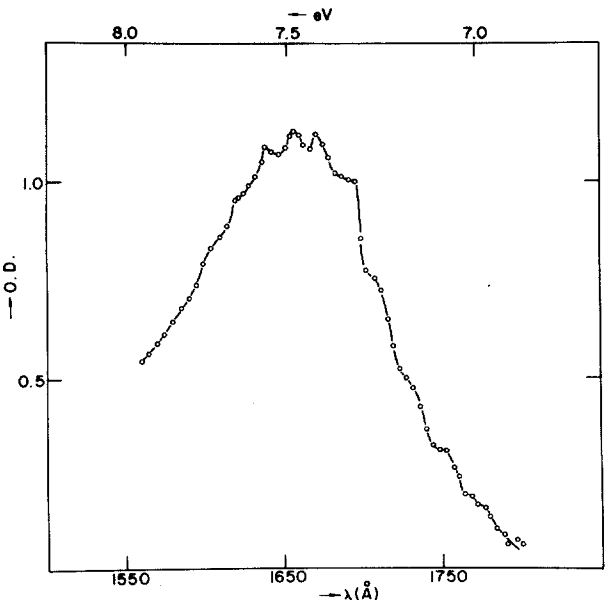

FIG. 3. Absorption spectrum of C_2H_4 in liquid krypton (resolution 2 Å).

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which are practically invariant under liquid–solid phase transition can be assigned to the $\pi \rightarrow \pi^*$ transition.

(d) The spectrum of C_2D_4 reveals a marked change by passing from the liquid Kr (Fig. 4) to solid Kr (Fig. 5). In the solid three new absorption bands appear which are not resolved in the liquid. These bands cannot be assigned to the intravelence excitation.

(e) New bands appearing for C_2H_4 in solid Kr (see Table II) which are not present in the liquid again cannot be assigned to an intravalence excitation.

Thus the identification of the vibrational components of the intravalence excitation of C_2H_4 in Ar(l), Kr(l) and Kr(s) is based on the following characteristics: (a) vibrational progression of ~600 cm^{-1}; (b) resolved bands appear only for C_2H_4 and not for C_2D_4; (c) similar linewidths and an identical vibrational structure in the solid and in the liquid; (d) a small liquid–solid spectral shift. The transition energies ascribed to the $\pi \rightarrow \pi^*$ transition of C_2H_4 in the rare gas matrices are summarized in Table II, where we have also presented the gas phase data obtained by us, which compare favorably with the original results of Mulliken and Wilkinson.[21] It should be pointed out that the absolute assignment of the gas phase vibrational levels is uncertain, so that the correspondence between a given line in the gas phase spectrum and in the matrix spectrum is only tentative (so that a uniform displacement of ~600 cm^{-1} is possible). Thus the gas matrix spectral shifts deduced from these data involve only an intelligent guess. On the other hand, we can safely compare spectra in different dense media, which for Kr(l) and Kr(s) were obtained for the same sample, and which for Kr and Ar were taken at known impurity concentrations (on the basis of the relative intensities of the vibrational bands). From these results we conclude that:

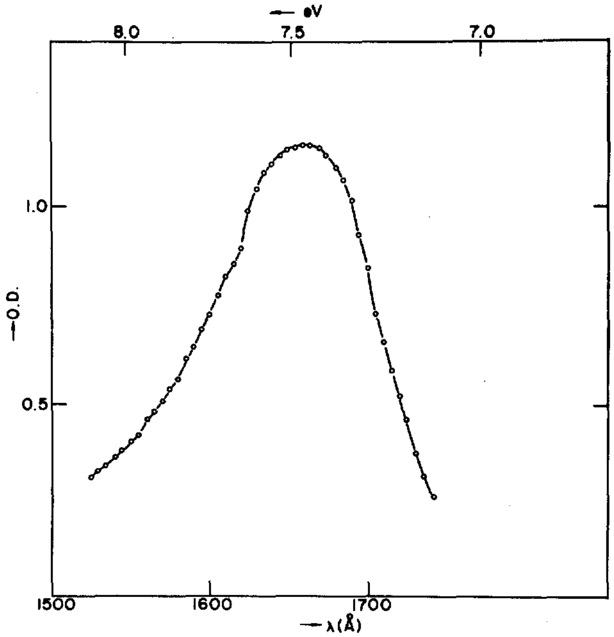

FIG. 4. Absorption spectrum of C_2D_4 in liquid krypton (resolution 2 Å).

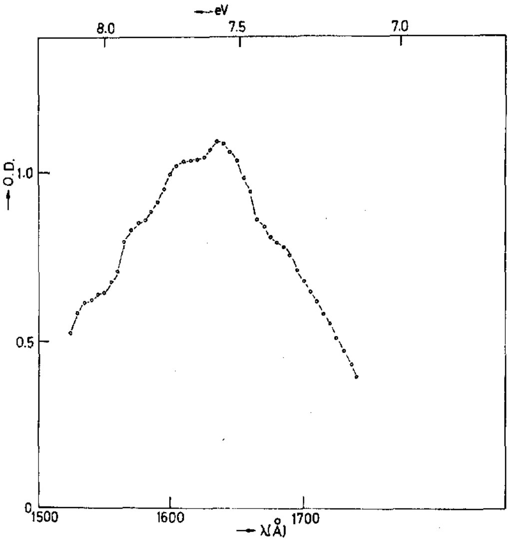

FIG. 5. Absorption spectrum of C_2D_4 in solid krypton (resolution 2 Å).

(1) A small red matrix-gas spectral shift is (tentatively) observed for the intravalence excitation. The spectral shifts are $\Delta\nu[\text{Ar(l)–gas}] = -400 \pm 50$ cm^{-1}, $\Delta\nu[\text{Kr(l)–gas}] = -600 \pm 100$ cm^{-1} and $\Delta\nu[\text{Kr(s)–gas}] = -600 \pm 100$ cm^{-1}. As already pointed out the spectral shift between Kr(s) and Kr(l) is negligibly small $\Delta\nu[\text{Kr(l)–Kr(s)}] = 70 \pm 100$ cm^{-1}, providing strong evidence for the assertion that the $\pi \rightarrow \pi^*$ transition does not involve appreciable charge expansion in the excited state.

(2) Six additional well resolved vibrational lines, which are not detected in the gas phase spectra, and which are assigned to the $\pi \rightarrow \pi^*$ transition were observed in the high energy range (1750–1620 Å) of ethylene in Ar(l), Kr(l), and Kr(s). In the gas phase these bands are presumably obscured by overlap with the strong $V \rightarrow R$ Rydberg transition, while in the dense media the Rydberg state is appreciably blue shifted, exposing these new vibrational components of the intravalence excitation.

(3) The dissociation energy of the V state (resulting in an excited CH_2 radical) was estimated by Wilkinson and Mulliken[21] to be located between 61 728 cm^{-1} (the energy corresponding to the maximum absorption in this region) and 57 071 cm^{-1} (the energy of the last distinguishable $\pi \rightarrow \pi^*$ band in the gas phase spectrum). According to our results in liquid argon matrix, the highest $\pi \rightarrow \pi^*$ vibrational component is located at

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TABLE II. The $N \rightarrow V$ transition energies of ethylene (free molecule and in solid and liquid rare gas matrices).

C_2H_4(g)				C_2H_4/Ar(l)		C_2H_4/Kr(l)		C_2H_4/Kr(s)	
Present work		Wilkinson and Mulliken							
(Å)	(cm^{-1})	(Å)	(cm^{-1})	(Å)	(cm^{-1})	(Å)	(cm^{-1})	(Å)	(cm^{-1})
				1580	63 290				
				1595	62 700				
				1613	62 000	1606	62 270		
				1630	61 350	1623	61 610		
				1647	60 720	1640	60 980		
				1664	60 100	1657	60 350	1653	60 500
				1681	59 490	1672	59 810	1670	59 880
				1700	58 820	1690	59 170	1689	59 210
				1721	58 110	1710	58 480	1708	58 550
				1740	57 470	1731	57 770	1725	57 970
				1765	56 660	1752	57 080	1750	57 140
1777	56 275	1776	56 306	1790	56 870	1773	56 400	1770	56 500
1805	55 402	1800	55 555			1795	55 710	1792	55 800
1831	54 615	1825	54 794			1820	54 950	1820	54 950
1855	53 908	1853	53 966			1844	54 230	1846	54 170
						1870	53 480		

63 290 cm^{-1}, indicating that a lower bound for the dissociation energy is ~64 000 cm^{-1}.

(4) No appreciable change occurs in the mean vibrational spacings for the $\pi \rightarrow \pi^*$ transition of C_2H_4 between the isolated molecule (790±100 cm^{-1}) and for the molecule doped in Ar(l), Kr(l), and Kr(s) (660±150 cm^{-1}).

(5) Unlike the case of the Schumann–Runge spectrum of O_2 in matrices, no significant negative anharmonicity effects can be observed for the higher vibrational components of C_2H_4 in the dense media. This difference can be possibly rationalized in terms of the contribution of several vibrational stretching and twisting modes to the effective vibrational progression of the ethylene molecule.

B. The Lowest Rydberg State in Dense Rare Gases

The identification of the lowest Rydberg transiton of ethylene in the dense rare gas matrices is based on the following features (see Sec. II):

(1) Vibrational progression (of the ν_2 totally symmetric stretching vibration) of 1200–1300 cm^{-1}.

(2) The same vibrational structure should be observed for C_2H_4 and for C_2D_4.

(3) The positions of the vibrational components of C_2H_4 and C_2D_4 in the matrix should not differ by more than 300 cm^{-1}, as is the case for the gas phase.

(4) The Rydberg transiton in liquid Kr should be appreciably red shifted relative to the corresponding solid.

(5) The Rydberg transition in liquid Ar should be appreciably blue shifted relative to liquid Kr.

(6) The linewidths of the vibronic components of the Rydberg transition should be appreciably sharpened in Kr(s) relative to Kr(l).

Turning now our attention to the absorption spectra of C_2H_4 and C_2D_4 in Ar(l), Kr(l), and Kr(s) in the spectral region 1650–1550 Å, (Figs. 3–5), we note the following features:

(a) From the spectrum of C_2D_4 in Ar(l) and in Kr(l), we can assert that the vibronic components of the first Rydberg transitons are not resolved in these liquid rare gas matrices. Thus in the liquid rare gases the linewidths of the $n=1$ Wannier ethylene impurity state exceed the vibrational spacing, so that $\Delta\nu_{n=1} \geq 2\nu_2 = 2600$ cm^{-1}. This result is not surprising, in view of the available experimental data concerning atomic, impurity states in liquid rare gases for the Xe $n=1$ state where it was found that $\Delta\nu_{n=1} = 1600 \pm 300$ cm^{-1} for Xe/Ar(l).[14]

(b) The center of gravity of the broad unresolved band of C_2D_4 in the liquid rare gas (see Table I) is appreciably blue shifted in Ar(l) relative to Kr(l). It should be mentioned at this point that the resolved vibrational components of the $\pi \rightarrow \pi^*$ transition superimposed on this continuous background are hardly affected by the change of the matrix (Table II). We may thus conclude that the shift of 1300 cm^{-1} of the maximum of the band of C_2D_4 and of C_2H_4 in Ar(l) relative to Kr(l) reflects the expected environmental shift on the first Rydberg transition.

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TABLE III. The Rydberg transition energies of ethylene.

C_2H_4(g)		C_2D_4(g)		C_2H_4/Kr(s)		C_2D_4/Kr(s)	
(Å)	(cm^{-1})	(Å)	(cm^{-1})	(Å)	(cm^{-1})	(Å)	(cm^{-1})
1742	57 405	1737	57 570	1540	64 940	1546	64 680
1729	57 837	1729	57 837	1573	63 570	1573	63 570
1702	58 754	1715	58 309	1606	62 270	1607	62 230
1689	59 206	1698	58 893	1638	61 050	1635	61 160
1664	60 096	1691	59 136				
1651	60 569	1678	59 594				
		1662	60 168				
		1655	60 422				
		1643	60 864				
		1629	61 387				
		1621	61 690				

(c) The spectrum of C_2D_4 reveals four new absorption bands in Kr(s) which are not resolved in Kr(l). These bands (Table III) which reveal a vibrational spacing of 1300 cm^{-1} and which are appreciably narrowed in the solid relative to the liquid are assigned to the lowest Rydberg transition in the solid Kr matrix.

(d) New band appearing in the spectrum of C_2H_4/Kr(s) which are not observed in C_2H_4/Kr(l) (Tables II, III) are again assigned to the vibronic components of the lowest Rydberg transition.

From the experimental results assembled in Table III we conclude that

(a) The lowest Rydberg state of C_2H_4 and C_2D_4 in solid Kr exhibits the 1200–1300 cm^{-1} stretching vibration characteristic of average spacing between the centers of the 0–$2\nu_4$ doublets in the gas phase $N \rightarrow R$ spectrum. In view of the line broadening in the Kr matrix the $2\nu_4$ progression merges into a single band. These results concur with previous thin film work by Katz and Jortner.[5]

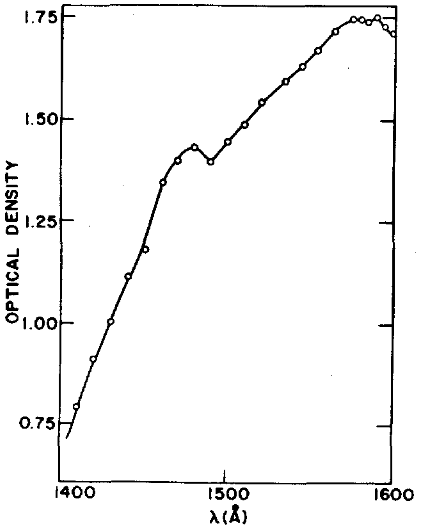

FIG. 6. Absorption spectrum of C_2H_4 in liquid argon in the range 1550–1450 Å (resolution 2 Å).

(b) The lowest Rydberg transition of C_2H_4 and C_2D_4 in Kr(s) is practically identical, as expected.

(c) The matrix-gas blue spectral shift for the lowest Rydberg state of C_2H_4 and C_2D_4 in Kr(s) at 80°K is 3200 ± 200 cm^{-1} confirming the theoretical arguments presented above. Katz and Jortner reported a blue spectral shift of 4000 cm^{-1} for the same system at 20°K. A temperature induced shift of 800 cm^{-1} for the molecular impurity state in the solid fits very nicely with the available experimental data on rare gas alloys.[25] Thus the Xe/Kr(s) system exhibits a temperature shift of 1100 cm^{-1} in the range 80–20°K.

(d) The linewidth of the vibronic components of the lowest Rydberg state of ethylene in Kr(s) at 80°K is of the order of the vibrational spacing, i.e.,

$$\Delta\nu_{n=1}(C_2H_4/Kr(s)) \sim 1000\text{–}1500 \text{ cm}^{-1}.$$

C. The $n=2$ Wannier State in Liquid Ar

The absorption spectrum of ethylene in liquid Ar in the spectral region 1580–1500 Å reveals a smooth continuous absorption decreasing towards higher energies. In the spectral range 1500–1400 Å (see Fig. 6) we have observed a new weak absorption superimposed on the continuum background. This broad absorption band at 1480 Å is tentatively assigned to the higher $n=2$ Wanner state of ethylene impurity in liquid Ar. In view of the limitations of the present experimental technique we were unable to study thick samples of ethylene in Kr in that spectral region, or to prepare C_2H_4/Ar(s) samples. Hence, the present assignment in this absorption is not conclusive. Subsequent work from this laboratory on ethylene in this rare gas film has conclusively demonstrated that this absorption around 1480 Å in Kr(s) is appreciably narrowed in the solid

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exhibiting a vibrational spacing of 1300 cm^{-1}, thus providing strong evidence for the assignment of the 1480 Å of $C_2H_4/Ar(l)$ to the $n=2$ Wannier molecular impurity state in liquid Ar.[26]

From this result we conclude that:

(a) Experimental evidence has been obtained that a molecular Wannier impurity state is amenable to experimental observation in liquid argon.

(b) Utilizing Eq. (1) we can estimate the ethylene impurity gap in liquid Ar. Taking $E_{n=2}=8.4$ eV and $G=3.2$ eV [for Ar/(l)] we obtain $E_g=9.2$ eV for the ionization potential of ethylene in liquid Ar.

(c) The polarization energy of liquid Ar by the ethylene positive ion can be obtained from Eq. (2) using $I_g=10.5$ eV so that $P_+=0.9$ eV. This value is quite reasonable, being lower than the P_+ value for Xe in liquid Ar.

V. CONCLUSIONS

In the present work we have attempted to provide a comprehensive study of extravalence excitations of a molecular impurity in rare gas liquids and solids. The main accomplishments of this work can be summarized as follows:

(a) From the experimental point of view we were able to prepare transparent thick (1 cm) ethylene doped krypton crystals which are suitable for vacuum ultraviolet spectroscopic studies. This work is complementary to previous studies in this laboratory on thick, low concentration rare gas alloys.[14] The use of thick doped rare gas crystals is superior to previous techniques utilizing thin films. Obvious advantages of the present technique involve direct comparison of impurity spectra in liquids and solids, and the wide temperature range available for such spectroscopic studies. The limitation of this sample preparation method involves the solubility problem of the impurity in the liquid and in the solid phase.

(b) From the point of view of general methodology we were able to advance several general criteria based on vibrational structure, vibrational isotope effects, matrix shifts, and line broadening, to identify extravalence molecular excitations of an impurity molecule in a simple matrix. These criteria were applied for the lowest Rydberg state of ethylene (the $n=1$ Wannier state).

(c) The lowest Rydberg state of ethylene and of ethylene-d_4 is amenable to experimental detection in solid krypton.

(d) In liquid Ar and liquid Kr the lowest Rydberg state is broadened by about a factor of 2–3 relative to the solid. Thus the widths of the vibronic components exceed their spacing and only an envelope of the Rydberg absorption band (further complicated by the $\pi\rightarrow\pi^*$ transition) is observed. Thus a typical organic aromatic molecule where the Rydberg state is characterized by a pronounced vibrational progression and overlaps intravelence excitation does not provide an adequate system for the study of the lowest Rydberg molecular state in simple liquids.

(e) We were able to provide the first experimental evidence for the observation of a $n=2$ Wannier state (originating from the molecular positive ion) of C_2H_4 in a liquid rare gas which bears no relation to the excited states of the isolated molecule.

Finally, we would like to point out that we were able to identify even higher excited states of ethylene and ethylene-d_4 in liquid Ar and in solid films of Ne, Ar, Kr, and Xe in the spectral region 1400–1250 Å. These states which overlap the direct transition to the conduction band of the matrix will be discussed separately.[26]

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