ARTICLES

ESR in Solid Hydrogen: Triplet Benzene and Naphthalene

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Benzene (C_6H_6, C_6D_6, $^{13}C_6H_6$) and naphthalene ($C_{10}H_8$, $C_{10}D_8$) molecules were trapped in solid normal hydrogen, normal deuterium, and for comparison, neon and argon. The triplet states of the aromatic hydrocarbons were excited by steady-state light sources, and their X-band ESR spectra observed. Lifetimes in those states were measured. Possible catalysis of the o-H_2 to p-H_2 conversion by these triplet states is discussed.

1. Introduction

Hydrogen forms a highly compressible quantum solid exhibiting large isotope effects and distinctive nuclear isomers.[1] It can then serve as an unusual and interesting matrix for the study of isolated molecules. This research is a continuation of the exploration of the electron spin resonance (ESR) spectroscopy of radicals trapped in solid H_2 and D_2 at 2 K. Our earlier published work in this area involved observation of the polycarbon molecules C_4, C_6, C_8,[2] and the transition-metal hydride and deuteride molecules VD_2,[3,4] NbH_4,[3] and BH_4.[5] Here we are extending the classic work of van der Waals and de Groot on the ESR of triplet benzene and naphthalene in rigid glasses[6,7] to the solid hydrogen environment. The only relevant past work that we have found is that by Thompson in 1965[8] in which he measured the phosphorescence of naphthalene in solid H_2 at 4.2 K and deduced a lifetime of 2.8 s.

ESR spectra of triplet benzene (C_6H_6, C_6D_6, $^{13}C_6H_6$), and naphthalene ($C_{10}H_8$, $C_{10}D_8$), have been measured in a series of matrixes n-H_2, n-D_2, and for comparison, Ne and Ar. Unfiltered steady irradiation provided by a high-pressure mercury lamp or xenon lamp was used for excitation. Interruption of the light allowed the lifetime of the ESR signal to be measured.

Our original concern in attempting to observe the excited triplet molecules in solid hydrogen was that the intense UV−visible light required to populate that state would thermally destroy the matrix. However, it was found that by pumping on the liquid helium refrigerant so as to maintain the hydrogen at ∼2 K, the matrix was usually stabilized during irradiation.

As is well-known, so-called normal hydrogen (n-H_2) at equilibrium at room temperature contains about 75% o-H_2 and 25% p-H_2. Upon cooling to low temperatures the o-H_2 slowly transforms to p-H_2, but this is catalyzed by the presence of free radicals.[1] One then presumes that benzene or naphthalene in a n-H_2 matrix at 2 K will act as a catalyst for this transformation when the hydrocarbon is excited to the triplet state. Evidence from $O_2(X^3\Sigma_g)$ studies[1,9] suggests that each triplet radical will rapidly be surrounded by p-H_2 molecules. This effect will more slowly spread throughout the solid, depending upon the concentration of the triplet and the temperature determining the rate of diffusion of o-H_2 molecules, and will stop when the radiation is shut off. One could, of course, avoid this transformation and its thermal effects by preparing matrixes using pure p-H_2, but we wished to see whether the ortho-to-para transition could possibly have an observable effect on the lifetime of the triplet.

Others are also studying the spectroscopy of species isolated in solid hydrogen: Miyazaki et al. have applied ESR largely to the detection and dynamics of H (or D) atoms produced by γ irradiation of solid hydrogen.[10,11] Fajardo et al. are studying dopants and their reactions by observations in the visible and ultraviolet;[12] Momose et al. are observing carbon clusters[13] and stable molecules and their photolysis products, using high-resolution spectroscopy.[14]

2. Experimental Section

The ESR apparatus and accompanying cryogenics have been previously described;[15,16] however, there have been some recent renovations. The older Bruker spectrometer has been replaced by an ESP 300 E. The copper rod (spatula-shaped, $3 \times 1 \times 32$ mm) was cooled by flowing liquid helium (Heli-Tran), pumped-on to attain a temperature of about 2 K. The cold rod was suspended in a Bruker X-band cavity (at room temperature), and the hydrocarbon/n-H_2 mixture (concentration 0.1 to 0.01 mol %) was passed up through the cavity and condensed on the rod. The flow was such that the background pressure was not greater than 10^{-5} Torr, and matrixes were usually prepared in about 10 to 15 min. The triplet state was excited by continuous irradiation with the unfiltered light from a 1 kw AH-6 high-pressure mercury arc (water-cooled) or an air-cooled 1 kw xenon lamp (Oriel) partially focused on the slotted side of the cavity. The intensity of the $\Delta M = 2$ signal at g $\cong$ 4 was monitored as a function of time after covering the lamp beam.

The hydrocarbons were pumped-on through several freeze and thaw cycles in order to remove oxygen. Benzene and naphthalene were purchased from Aldrich and isotopically substituted compounds from Cambridge Isotopes. Hydrogen and argon were standard research purity from BOC, neon was
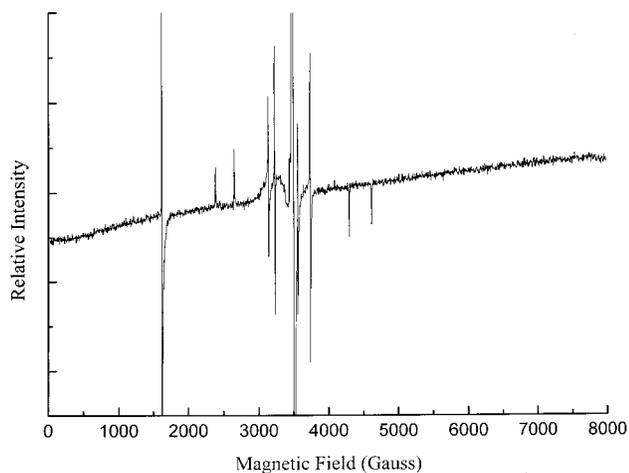

Figure 1. Electron spin resonance spectrum of deuterated naphthalene ($C_{10}D_8$) in its excited triplet state in solid n-H_2 (concentration = 0.1%) at 2 K. A large impurity signal occurs at g $\cong$ 2.0 (at ~3500 G) with H atom signals separated by ~500 G (ν = 9.8065 GHz).
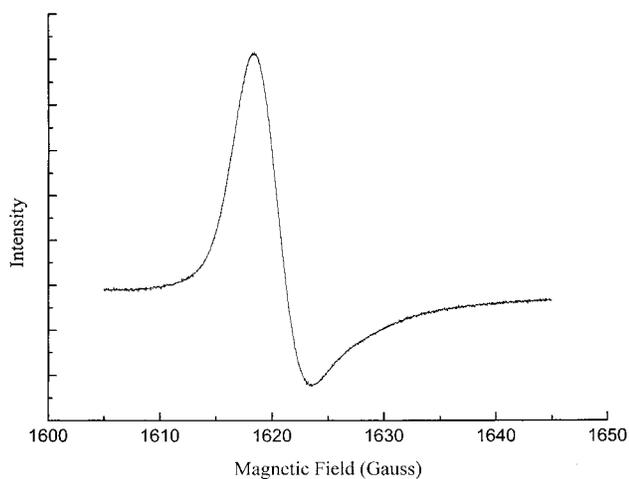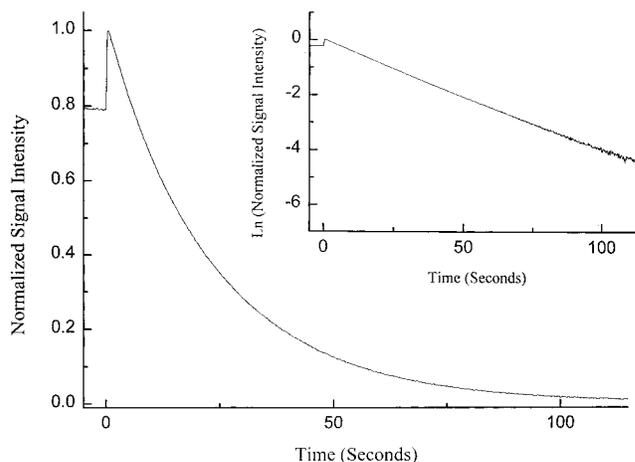

Figure 3. The intensity of the $\Delta M = 2$ signal in Figure 2 as a function of time after the exciting light beam was interrupted. The inset in the upper right-hand corner is a natural log plot of the signal vs time.
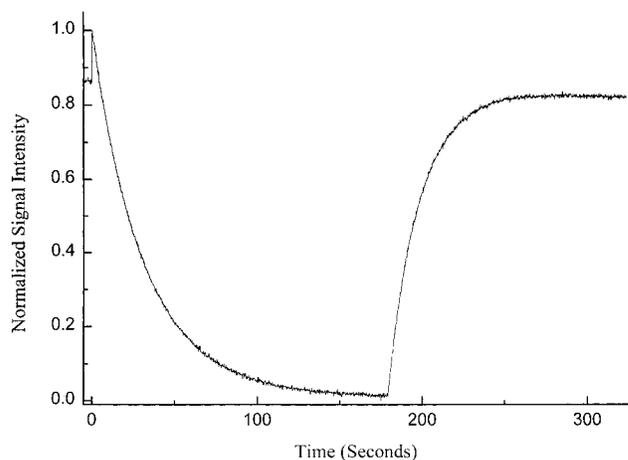

Figure 2. The $\Delta M = 2$ signal at 1620 G in Figure 1.

Figure 4. The decay signal shown in Figure 3 along with the recovery signal after the shutter covering the lamp was removed.

research purity from Matheson, and deuterium purchased from Cambridge Isotopes was 99.8% pure.

3. Results

Figure 1 shows the ESR spectrum of triplet *d*-naphthalene at a concentration of 0.1% in n-H_2 during irradiation with the xenon lamp. There is a large impurity signal at $g = 2.0$ and the two adjoining bands spaced 500 G apart are due to H atoms. Both $\Delta M = 1$ and $\Delta M = 2$ signals[7,17] are clearly observed. The $\Delta M = 2$ band at 1620 G is shown on an expanded scale in Figure 2. When the magnet field is set on the peak of this band and the light radiation is interrupted, the band intensity as a function of time is shown in Figure 3. The inset in that figure shows the natural logarithm of the intensity as a function of time, indicating that the decay is close to exponential. A lifetime $\tau = 23$ s was derived. By covering and uncovering the lamp beam the decay and recovery signals were obtained as shown in Figure 4. Variation of the concentration within the range 0.1 to 0.01 mol % did not change the measured lifetime of decay. Variation of the exciting radiation, Hg-arc or Xe-lamp, did not have a significant effect upon the observed spectra.

The ESR spectra of the benzenes were weaker than the naphthalenes, because the absorption $S_1 \leftarrow S_0$ occurs further in the ultraviolet than naphthalene (39 000 vs 33 000 cm^{-1}) where the exciting lamps are less effective. The spectrum for d-benzene
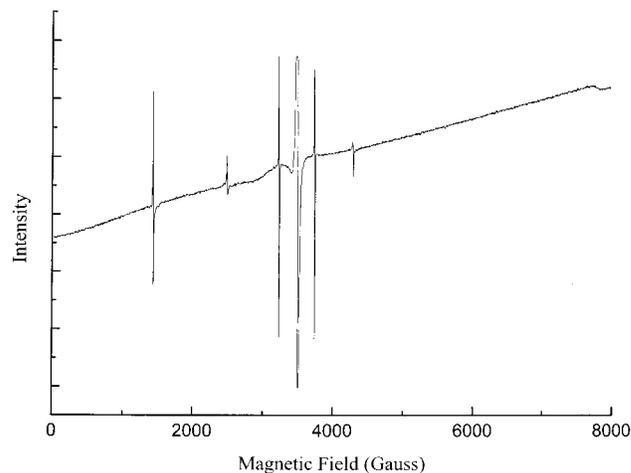

Figure 5. Electron spin resonance of deuterated benzene (C_6D_6) in its excited state in solid n-H_2 (concentration = 0.1%). A large impurity signal occurs at g $\cong$ 2.0 with H atom signals separated by ~500 G (ν = 9.8065 GHz).

in H_2 is shown in Figure 5 with an expanded view of the $\Delta M = 2$ transition in Figure 6. Although the spectrum in Figure 5 is weak, the $\Delta M = 1$ lines show no apparent indication of $E \neq 0$ (the so-called "parallel" z lines are always weak and are not observable in any of these ESR spectra).[17] This suggests that the triplet state of benzene in the hydrogen matrixes at 2 K has
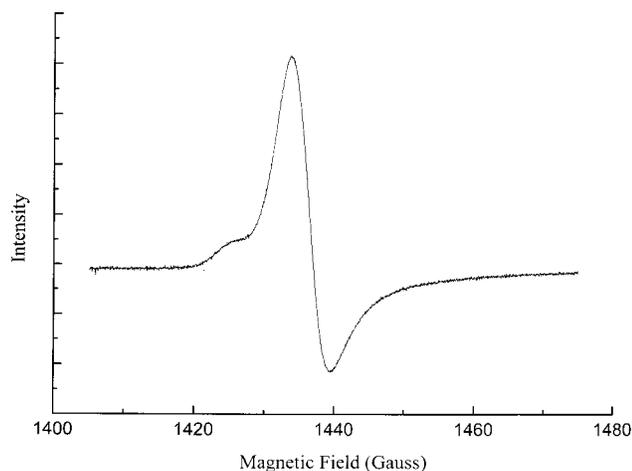
Figure 6. The $\Delta M = 2$ signal at 1435 G in Figure 5. The low-field shoulder is presumably another site in this unannealed matrix.

TABLE 1: Lifetime of the Triplet State of Naphthalene ($C_{10}H_8$) in Various Matrixes at 2 K

matrix	H_{min} (G)	ν (GHz)	g	our τ (s)	other τ (s)
n-H$_2$	1622.8	9.80657	4.318	2.3(1)	2.8[a]
n-D$_2$	1622.4	9.80673	4.319	2.5	
Ne	1617.3	9.80643	4.332	2.4	
Ar (4 K)	1621.1	9.80606	4.322	1.8	1.7[a]

[a] Ref 8.

TABLE 2: Lifetime of the Triplet State of Deuterated Naphthalene ($C_{10}D_8$) in Various Matrixes at 2 K

matrix	H_{min} (G)	ν (GHz)	g	our τ (s)	other τ (s)
n-H$_2$	1620.0	9.80600	4.325	23(1)	
n-D$_2$	1620.4	9.80654	4.324	30	
Ne	1613.7	9.80565	4.342	28	
Ar (4 K)	1619.8	9.80609	4.325	16	18[a]

[a] Ref 8.

TABLE 3: Lifetime of the Triplet State of Benzene (C_6H_6) in Various Matrixes at 2 K

matrix	H_{min} (G)	ν (GHz)	g	our τ (s)	other τ (s)
n-H$_2$ 0.1%	1444.4	9.80625	4.851	20(1)	
n-D$_2$	1440.8	9.80645	4.863	20	
Ne	1430.1	9.80615	4.800	16	
Ar (4 K)	1433.4	9.80597	4.888	16	16[a]

[a] Ref 19.

TABLE 4: Lifetime of the Triplet State of Deuterated Benzene (C_6D_6) in Various Matrixes at 2 K

matrix	H_{min} (G)	ν (GHz)	g	our τ (s)	other τ (s)
n-H$_2$	1435.8	9.80651	4.880	37(1)	
n-D$_2$	1434.5	9.80645	4.884	32	
Ar	1426.8	9.80634	4.911	27	26[a]

[a] Ref 19.

at least trigonal symmetry, i.e., without the distortions observed by de Groot and van der Waals.[7]

Similar spectra to those in the figures were observed for the benzene and naphthalene molecules in various matrixes. The results are given in Tables 1−5. The measurements in n-H$_2$, n-D$_2$, and Ne were at 2 K, those in solid Ar at 4 K. The $\Delta M = 1$ transitions were not always observed, or observed only weakly, and only the strong $\Delta M = 2$ bands are listed in the tables.

4. Discussion

One expects, because of its open structure and weak intermolecular interactions, that the environment for isolated

TABLE 5: Lifetime of the Triplet State of ^{13}C-Substituted Benzene ($^{13}C_6H_6$) in Various Matrixes at 2 K

matrix	H_{min} (G)	ν (GHz)	g	our τ (s)
n-H$_2$	1444.8	9.80648	4.850	21(1)
n-D$_2$	1439.4	9.80614	4.868	21(1)
Ar (4 K)	1433.9	9.80517	4.886	16

molecules in solid hydrogen would be as gaslike as could be found among matrixes or glasses. This would be judged by observing narrow lines and relatively long relaxation times for the $S_o \leftarrow T_1$ transition. These are compared for the five molecules C_6H_6, C_6D_6, $^{13}C_6H_6$, $C_{10}H_8$, and $C_{10}D_8$ in solid n-H$_2$, n-D$_2$, Ne, and Ar in Tables 1−5. Also included, where available, are the measurements of others, as given by Thompson,[8] Robinson, Frosch et al.,[19−22] and Birks,[23] of the phosphorescence lifetimes in solid argon at 4 K. These are in good agreement with our ESR values.

One notes in Figures 3 and 4, an upward spike, i.e., an increase in intensity of the $\Delta M = 2$ ESR signal, just after the shutter was placed across the exciting light beam. This is reproducible and is attributed to $T_2 \rightarrow T_1$ relaxation, thereby increasing the population of the T_1 state and the ESR signal in that state. Although there is no overlap of the $T_1 \leftarrow S_o$ and $T_2 \leftarrow T_1$ absorption bands in these aromatics,[18] the unfiltered light is intense for both transitions and can be expected to lead to some triplet−triplet absorption. The $T_2 \rightarrow T_1$ relaxation is very fast, $\sim 10^{12}$ s^{-1}.[24]

Lifetimes. The relaxation of $T_1 \rightarrow S_o$ in aromatics is determined by radiative and nonradiative rates, where the latter dominates in naphthalene. The theory of radiationless transitions,[20,22] as discussed thoroughly by Robinson et al.[20−22] and Siebrand,[25] attributes this relaxation to Franck−Condon overlap of the vibrational wave function in the two electronic states governed by the anharmonic distortions of the C−H (and C−D) stretching modes. This explains the large increase in τ in the perdeuterated molecules. Since it is intramolecular, it is not surprising that the lifetimes in H$_2$ and D$_2$ are close to each other. Even with the large mass change from H$_2$ to D$_2$, the spin−orbit effects are negligible and a so-called "external heavy atom" effect is not expected. The $^{13}C_6H_6$ molecule was researched out of curiosity, since ^{13}C would be expected to affect the C−H vibrational modes. The isotopic substitution does yield $\tau = 21$ s, i.e., between 20 s for C_6H_6 and 37 s for C_6D_6. This small a shift is not unexpected since the vibrational modes involve largely motions of the lighter atoms.

An attempt was made to see whether the measured ESR lifetime of deuterated naphthalene in n-H$_2$ was different immediately after trapping relative to a later time when o-H$_2$ had presumably been catalyzed by the triplet to form p-H$_2$. However, the decay curve could not be observed sooner than about 80 s after first exciting the triplet. Over the next 1/2 h no change in the decay was detected. If there is a catalytic effect it presumably occurs within the initial period, and all of our lifetime measurements are then being made of radicals trapped in a p-H$_2$ environment. (Maintaining a hydrogen matrix at 2 K for a longer period is not feasible in our present apparatus, and would also require a large expenditure of liquid helium.) We did not make any measurements on matrixes prepared using "pure" p-H$_2$.

Catalysis of the o-H$_2$ to p-H$_2$ Conversion. Although a definitive analysis is not possible, it is interesting to consider the catalysis of conversion which presumably will be effected by the triplet states of these aromatic molecules in n-H$_2$. This conversion is a considerable heat effect since the $E_{J=1} - E_{J=0}$ energy difference is 340 cal mol^{-1} of o-H$_2$;[1] whereas the heat

of fusion of solid H_2 is only 28 cal mol^{-1};[26] or perhaps more pertinent here, only about 4 cal are required to heat a mole of solid n-H_2 from 2 to 10 K where its vapor pressure is about 2 Torr.[26] Experimentally there have been no indications here of the conversion by changes in temperature, pressure, or lifetime measurements on these dilute matrixes. Of course, the ultimate experiment will be the direct determination of the ortho-to-para ratio in the final matrix solid or gas.

Wigner's catalytic mechanism[27] requires the triplet/o-H_2 interaction to be such that the two ends of the o-H_2 molecule feel different magnetic fields. Wigner's theory has been questioned as predicting a much weaker catalytic effect ($\sim10^{-2}$ times) than those measured (for O_2, for example). An alternative theory involves the mixing of triplet character into the H_2 wave function through configuration interaction.[28,29] Although very small, this mixing can account for the conversion in the $O_2-$$H_2$ (linear) complex. Both catalytic mechanisms are short range and require intimate contact between the aromatic π system and o-H_2 molecules. The effectiveness of the triplet states in these aromatics, relative to O_2, NO, NO_2, in effecting the conversion is the interesting question.

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