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The Fluorescence of *N*-Phenylpyrrole in an Argon/Acetonitrile Matrix

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N-Phenylpyrrole (PP) was studied in an argon matrix at 14−30 K. The absorption and fluorescence excitation spectra are structureless, while the emission spectrum shows distinct vibrational structure. When a small amount of the polar molecule acetonitrile is added to the PP/argon matrix, UV excitation leads to two separate emission bands the relative intensity of which is strongly excitation wavelength dependent. Control experiments using a nonpolar molecule (ethylene) and dimethylaminobenzonitrile help to assign the spectra. Both emission bands are assigned to transitions from an electronically excited charge-transfer state that has two distinct minima.

I. Introduction

The UV absorption and emission spectra of PP were studied in various environments and found to exhibit some unique features. The most conspicuous one is the fact that in polar solvents the molecule exhibits dual fluorescence from two minima on the S_1 surface.[1−4] PP thus belongs to the class of molecules exhibiting dual fluorescence, first observed for dimethylaminobenzonitrile (DMABN).[5] The spectral properties of DMABN were extensively studied experimentally [reviews, refs 6 and 7] and theoretically [see, for instance, refs 8 and 9], making it a standard "parent" molecule that is used to discuss properties of other benzene derivatives that display dual fluorescence. It is therefore instructive to discuss the properties of PP in comparison to those of DMABN while outlining the rationale for the present study.

In DMABN, the "normal" fluorescence spectrum, observed in nonpolar solvents, bears an approximate mirror image relationship to the absorption spectrum; it is assigned to emission from a locally excited state, commonly termed the B state. The "anomalous" fluorescence, which appears only in polar solvents and is strongly red-shifted with respect to the absorption spectrum, is assigned to a charge-transfer (CT) state, which is correlated with the so-called A state (S_2 in the isolated molecule). The B and A excited states are derived from the 1^1B_{2u} and 1^1B_{1u} states of benzene, respectively, to which electric dipole transitions from the ground state are forbidden. In substituted benzene molecules, the transitions are partially allowed; notwithstanding, the transition to the primarily covalent B state is much more forbidden than the transition to the primarily ionic A state. (These states are sometimes labeled as the L_b and L_a states in substituted benzene derivatives). For both PP and DMABN, we shall use the B and A state designation to characterize the electronic nature of the state. Their relative energy ordering may vary, depending on the environment.

In the gas phase, the room-temperature fluorescence spectrum of PP is apparently void of vibrational structure, making it difficult to assign. In the cold jet, both excitation and emission spectra display extensive vibronic structure.[10,11] Near the origin of the S_0−S_1 transition, the spectrum is dominated by a progression in the torsional mode around the C_{phenyl}−N bond. As in the case of DMABN, the S_1 excited state was assigned as the covalent excited B state derived from the 1^1B_{2u} state of benzene. However, the separation between the 1^1B and the 1^1A states in PP is small, about 500 cm^{-1},[11] and the spectrum becomes more complicated at fairly low excess energies, as absorption into the more-allowed 1^1A state sets in with the possible participation of other excited states.[11] In contrast, the absorption spectrum of DMABN is simpler; because the S_1−S_2 gap is much larger, up to about 4000 cm^{-1} excess energy, the spectrum may be assigned to the B state only[12−14]. Some properties of PP and DMABN[15−18] are listed in Table 1, which helps to reveal the similarities and differences between these two molecules.

TABLE 1: Some Properties of PP and DMABN[a]

	DMABN	PP
GS[b] twist angle (deg)	∼0[12]	38.7[10]
GS dipole moment (D)	6.6[15]	−1.39[16]
B state dipole moment (D)	5.8[17]	−3[4]
CT state dipole moment (D)	16[17]	11[4]
B state gas-phase origin (eV)	∼4.0[13,14]	4.4[10]
A state gas-phase origin (eV)	∼4.5[18]	∼4.45[11]
A−B energy gap (eV)	∼0.5[18]	∼0.05[11]

[a] The energies of the S_1 states are precisely known from jet studies. The energy data for the A state are estimates based on less accurate measurements; the error may be up to 0.2 eV. For the purposes of this paper, in particular, the comparison of DMABN and PP, these estimates are sufficient. [b] GS denotes the ground state.

Several suggestions as to the nature of the CT state of DMABN and other amino derivatives of benzene such as PP were proposed. Currently, two models appear to be the most compatible with experimental results: a twisted charge-transfer state (TICT)[19] and a planar charge-transfer state (PICT).[20] We have recently suggested a physical model for the TICT state based on the properties of the L_b and L_a states of benzene.[21] In this model, the first excited state of these molecules in the gas phase (the B state) is a locally excited (LE) state of pure covalent nature derived from the 1^1B_{2u} (L_b) state of benzene. The second excited state (the ionic A state) assumes a charge-transfer character due to the electron-donating power of the pyrrolo moiety. It was shown that two minima could exist on the A

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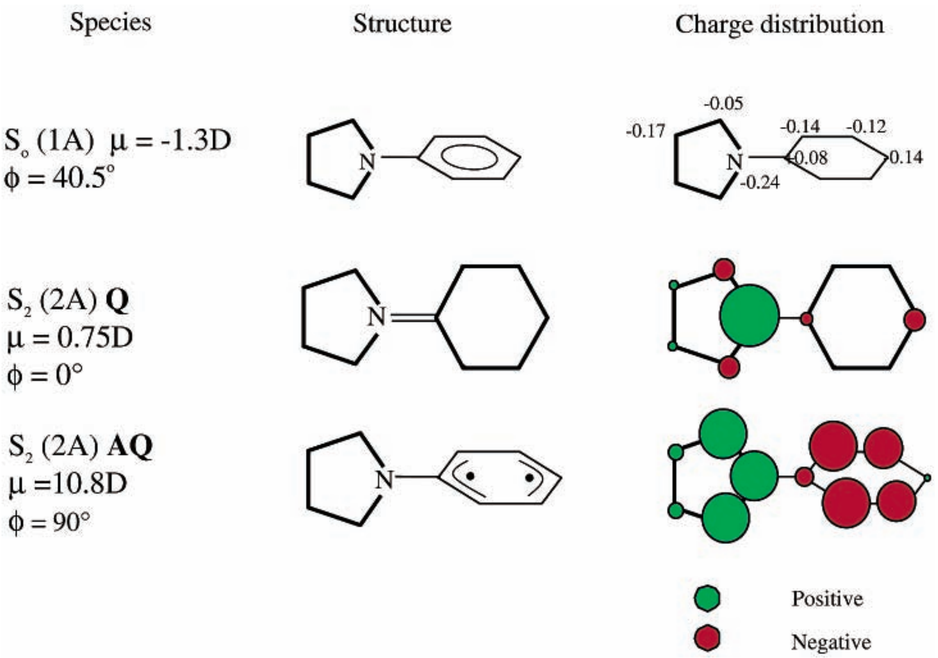
SCHEME 1: A Schematic Representation of the Structure and Charge Distribution of PP in the Ground State (Top), the Quinoidal Form of the A State (Middle), and the Antiquinoidal Form of the A State (Bottom)[a]



[a] ϕ is the torsional angle at the minimum of each state; μ is the dipole moment in D. The charge distribution is from ref 21; the size of the circle is proportional to the charge of the atom. The color code is green = positive charge and red = negative charge.

state potential energy surface because of a quinoidal or antiquinoidal distortion. In the Q form, the phenyl ring assumes a quinoidal (Q) structure and the two rings become coplanar as the CN bond shortens. This form corresponds to the PICT model. In the AQ form, the phenyl ring is stretched to an antiquinoidal structure: the two central bonds elongate, as does the CN bond. This form turns out to be most stable when the phenyl and pyrrole rings are perpendicular to each other. The resulting twisted form corresponds to the TICT model. Scheme 1 shows schematically these distortions and the resulting charge distributions.[21] The Q form of PP is calculated to be lower in energy in the gas phase but has a smaller dipole moment. Therefore, in a highly polar environment, the AQ minimum may be found at a lower energy than the Q one. Moreover, in that environment, the polar A state may be stabilized to a larger extent than the covalent B state and become S_1. As seen from Scheme 1, the calculated charge distribution in the two minima is different—the charge alternates along the molecular frame in the Q form and is concentrated in the rings in the AQ form.

Clusters formed in a supersonic jet are considered as intermediate species between gaseous molecules and condensed matter. No data on PP clusters are available at this time, but reports on DMABN are available and present a somewhat confusing situation.

It was shown in ref 22 that DMABN forms clusters with polar molecules such as acetonitrile (AN) in a supersonic jet. Some clusters exhibit dual fluorescence, in contrast with the absence of the “anomalous” fluorescence in the case of the isolated molecule. Specifically it was shown that clusters containing up to four AN molecules display LE emission only while clusters with five and more AN molecules show also CT emission (a separate peak centered at 425 nm). This finding was explained as indicating that at least five nearest AN neighbors are required to stabilize the CT state to below the energy of the B state. Howell et al.[23] reported a red-shifted band peaking at 414 nm, which they tentatively assigned to a solvated DMABN dimer. In an apparent contrast, Saigusa et al.,[24] using similar apparatus, reported different emission spectra. The fluorescence of small DMABN/AN clusters was the same as that in ref 22, but as the acetonitrile concentration was increased, only a small red shift was observed, and no distinct peak at 425 nm could be observed. The authors speculate that the latter peak could be due to AN-solvated DMABN dimers but suggest further investigations.

Matrix isolation is a second experimental technique that can probe molecular clusters at low temperatures.[25] In this communication, we report what we believe is the first measurement of the fluorescence of PP in a cryogenic argon matrix. The goal of these measurements was to find out whether a CT-type emission band could be observed in a rigid matrix under conditions that strongly impede the torsional motion. PP was chosen for this work for several reasons: it was hoped that the close proximity of the two electronic states might help to observe dual emission even in the rigid environment of solid argon. The absence of two methyl groups should help in simplifying the observed spectra and make it easier to simulate matrix isolation by molecular dynamics methods.[26] The relatively long decay time measured in the supersonic jet (~20 ns)[11] was considered as promising strong fluorescence also in the matrix. Indeed, it was found that codeposition of PP with a small amount of acetonitrile in an argon matrix led to the observation of two well-separated emission bands upon UV excitation. This dual fluorescence is much more pronounced than that observed for PP dissolved in acetonitrile at higher temperatures[4] and is discussed in terms of the CT model.

II. Experimental Section

PP (99%) was obtained from Aldrich and used as received. Samples were deposited on a BaF_2 window held at the tip of an APD 202 closed-cycle helium cryostat. PP (Aldrich) vapor was premixed with argon (99.999%, typical guest/host ratio 1:1000) in a stainless steel feed line and deposited at 25 K through a needle valve at a rate of about 3 mmol/h. Acetonitrile (Aldrich, 99.5%) and ethylene (Matheson, 99.5%), used as

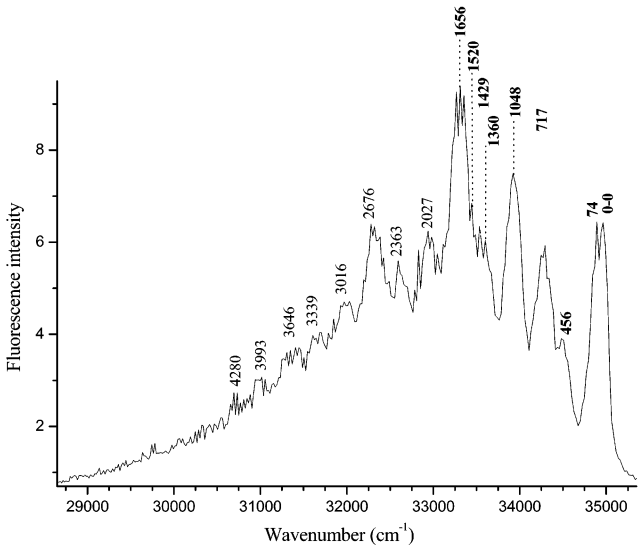


Figure 1. The fluorescence emission spectrum of PP in an argon matrix. The host/guest ratio is about 1:1000; the matrix was deposited and the spectrum was taken at 25 K. Spectral resolution is 4 Å.

received, were premixed with argon in the gas phase at the desired ratios before being deposited on the cold window in the same manner.

Preliminary absorption spectra were measured with a xenon arc/monochromator combination, at a resolution of 8 cm^{-1}. Some absorption spectra were scanned using a dye laser (Lambda Physik FL3002 pumped by an excimer laser) at 0.4 cm^{-1} resolution. Emission spectra were measured with 10−40 cm^{-1} resolution using a Spex model 1702/4.75 m spectrometer. Detection was by Hamamatsu R562 or R1332 photomultiplier tubes connected to a digital oscilloscope (Tektronix model 2430). The oscilloscope was interfaced to a Pentium IV personal computer by a GPIB card.

III. Results

The absorption spectrum of PP in an argon matrix is broad and structureless and bears a strong resemblance to liquid-phase spectra.[10] In contrast, the *emission* spectrum in an argon matrix shows clear vibrational structure. Figure 1 shows a typical emission spectrum, obtained upon excitation at 275 nm, and Table 2 lists the observed peaks and their assignments.[27−29] Attempts to obtain an excitation spectrum led to a broad and structureless spectrum; no vibrational structure could be observed, except for an initial rise leading to a local maximum at 284.1 nm. This feature of the excitation spectrum was taken as the 0−0 band.

Addition of small amounts (0.5−2%) of acetonitrile (CH_3CN, abbreviated as AN) to the deposition mixture led to a remarkable change of the emission spectra observed at 25 K. An example is shown in Figure 2 with 1% acetonitrile added. Excitation in the range of 270−284 nm resulted in a dual fluorescence with two broad bands peaking at about 300 and 345 nm, respectively. Excitation at λ_{exc} > 284 nm led to the appearance of a single broad emission band at around 350 nm. Excitation could be extended to 295 nm and beyond, namely, to much lower energies than required for the argon-trapped PP. No vibrational structure could be discerned in the excitation spectrum, and no attempt was made to determine the origin of the band. At shorter excitation wavelengths, the red-shifted band became weaker till it was hardly noticeable at 270 nm and beyond. Data obtained with other concentrations of acetonitrile were similar, but below 0.5%, the red-shifted band was barely observable.

TABLE 2: The Observed Emission Peaks in the Fluorescence Spectrum of PP in an Argon Matrix at 14 K[a]

band position	relative energy	DFT[b]	tentative assignment[c]	remark[d]
34 965	0			origin band
34 891	74	65	torsion[10]	a
34 509	456	428	Ph-N in-plane bend	b
34 251	717	710	W4 (out of plane ring def.)	c
33 924	1048	1051	pyrrole moiety	d
33 605	1360	1358	ν_s(Ph-N), W3 (CH in-plane bending)	e
33 538	1429	1436	pyrrole moiety	f
33 444	1519	1509	W19a (CC), W18a	g
33 311	1656	1656	W8a (CC)	h
32 936	2029		overtone	d*2
32 600	2365		combination	c + h
32 282	2683		combination	d + h
31 933	3032		overtone	d*3
31 609	3356		overtone	h*2

[a] Energies are in wavenumbers. [b] At the BLYP/6-31G(d) level of theory. [c] Based on the DFT calculation, on the assignment of DMABN,[27] and on comparison with ground-state 4-(pyrrol-1-yl)benzonitrile (PBN).[28] Benzene ring vibrational modes are indicated using Wilson's notation,[29] designated with W prefix. [d] Fundamental bands are symbolized alphabetically; overtone and combination bands are designated according to their fundamental components.

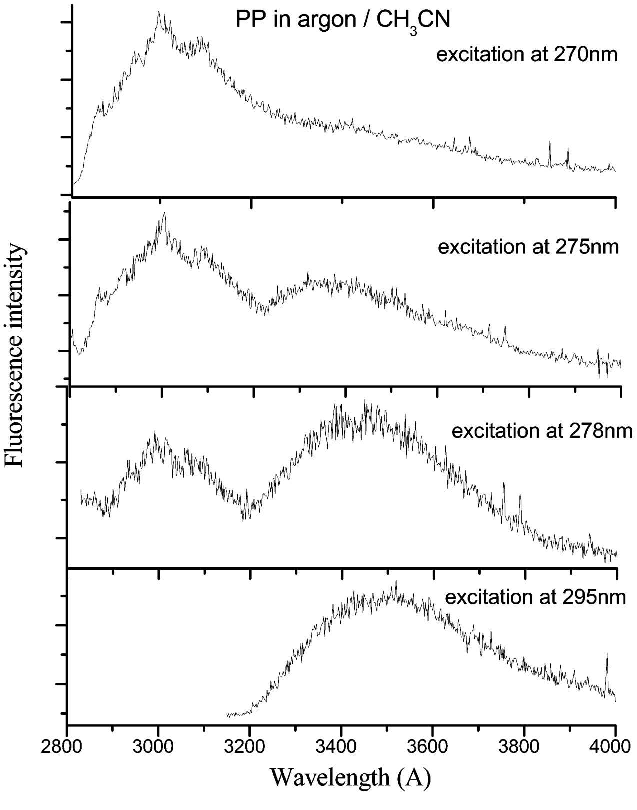


Figure 2. The fluorescence emission spectra of PP in a 100:1 argon/AN matrix at 25 K. The excitation wavelengths were (top to bottom) 270, 275, 278, and 295 nm.

Several control experiments were carried out to elucidate the origin of the red-shifted emission band. In one, a small amount of ethylene was added to the PP/argon mixture instead of AN. The emission spectrum at 25 K consisted of a single band slightly shifted to the red from the neat argon matrix spectrum

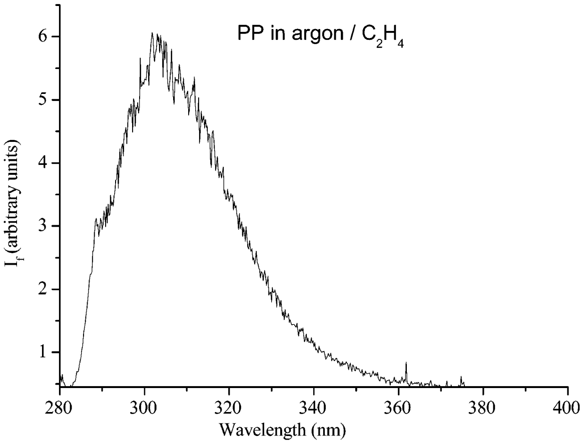


Figure 3. The fluorescence emission spectrum of PP in a 20:1 argon/ethylene matrix at 25 K. The excitation wavelength was 301.8 nm.

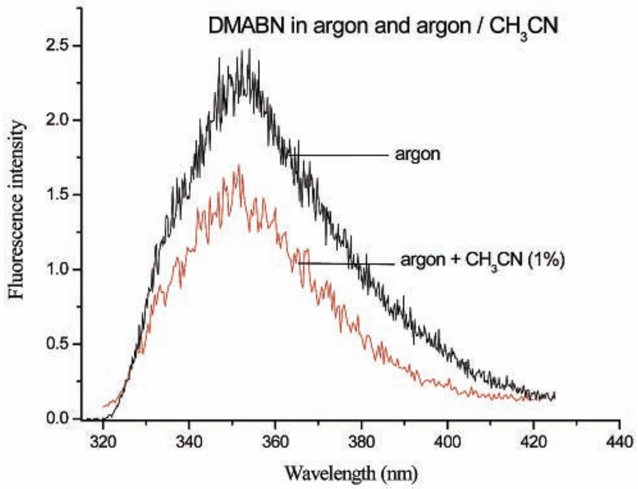


Figure 4. The fluorescence emission spectrum of DMABN in a 100:1 argon and argon/AN matrixes at 25 K. The excitation wavelength was 310.0 nm for the neat argon matrix (top curve) and 311.8 nm for the AN-doped matrix (bottom curve). The spectra are slightly shifted vertically for clarity.

as shown in Figure 3. The emission spectrum was independent of the excitation wavelength; in addition, it did not change as the concentration of ethylene was increased up to 6%.

Another control experiment was run with DMABN in an acetonitrile-doped matrix (Figure 4). The emission spectra were very similar to the spectra in a neat argon matrix; no red-shifted emission band was observed at any excitation wavelength, despite a very meticulous and extensive search.

The possibility that irradiation of PP in the presence of AN in a low-temperature matrix might yield a stable photochemical product that emits around 345 nm was also examined. This was done by UV irradiation of the PP/AN/argon matrix and periodically checking the IR spectrum every few minutes. No change in the spectrum could be detected after irradiation for over an hour, a period exceeding the time necessary to record the emission spectrum.

IV. Discussion

IVa. PP in an Argon Matrix. The emission spectrum of PP in an argon matrix displays a clear vibrational structure, while the absorption and excitation spectra are found to be structureless, notwithstanding the high resolution employed (0.4 cm^{-1}). The vibrational structure conforms with the ground-state vibrational levels; some assignments are shown in Figure 1 and Table 2. The absence of vibrational structure in the excitation spectrum is not a universal occurrence for substituted benzene molecules in an argon matrix. For instance, aniline[30] and *n*-propylbenzene[31] were recently found to exhibit a clear vibrational structure in an argon matrix in both emission and excitation. Moreover, a vibrational structure was also found for PP in a supersonic jet in both emission and excitation spectra.[10,11]

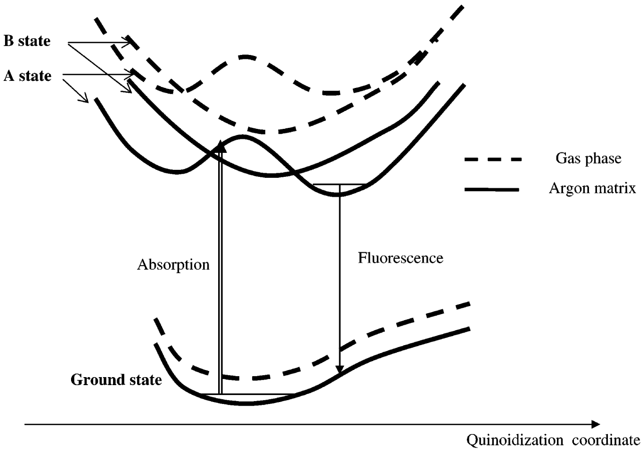


Figure 5. A schematic energy level diagram of PP in an argon matrix and in the gas phase plotted as a function of the quinoidization coordinate (see ref 21). In the gas phase, the B state is slightly lower that the A state. In an argon matrix, one of the minima of the A state is lower than the B state. Emission is mainly from the A state.

A tentative explanation for the absence of vibrational structure in the excitation spectrum may be offered on the basis of the model discussed in ref 21. The spacing between the B and the A states is quite small in the gas phase (about 500 cm^{-1}). Because of the polarizability of the argon atoms, the more polar A state is expected to be better stabilized than the nonpolar B state in an argon matrix. The two states might switch their positions so that the A state becomes S_1. This ionic-type state has local minima at the quinoid and antiquinoid structures, in which a charge-transfer took place. Calculations[21] show that the geometries of the Q and AQ forms of the CT state are different from that of the ground state of PP. Consequently, at the Franck−Condon region, there is a gradient toward the minimum, and the vibrational levels are closely spaced. Thus, immediately after excitation of the A state, the system relaxes into one of these minima, which is the fluorescent state. At this point, we cannot determine which of the two is preferred in an argon matrix. A schematic energy level diagram for PP in an argon matrix is shown in Figure 5. The absence of structure in the excitation spectrum is probably due to the interaction between the A and B states, which are very close together and interact via a conical intersection. The resulting potential surface is very shallow along the torsional angle (rotation of the pyrrol ring with respect to the phenyl), leading to a dense manifold of vibrational levels. Moreover, each level is broadened by interactions with the phonons of the matrix. Thus, a broad and structureless electronic absorption spectrum is observed.

This scenario is supported to a certain extent by the observed matrix shift of the transition. The gas-phase 0−0 band is at 35 493 cm^{-1}.[10] The matrix value is 34 965 in emission and 35 200 cm^{-1} in excitation. If an average of 35 080 is used, the matrix shift is approximately 410 cm^{-1}. This is a very large value for a forbidden transition; the X−B transition has an oscillator strength of about 10^{-3}.[32] The argon matrix shift for such transitions is on the order of 100 cm^{-1}, as observed, for

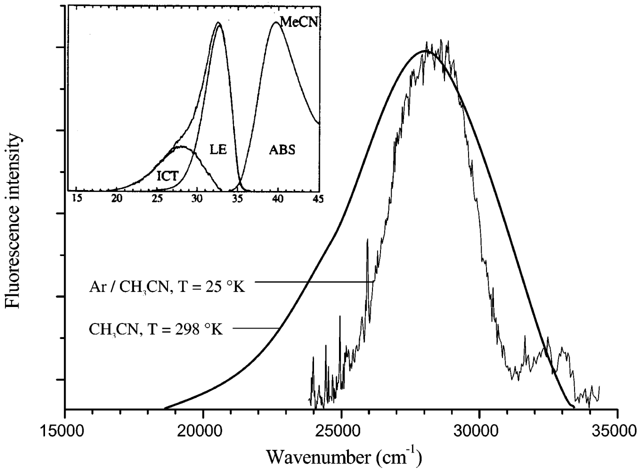


Figure 6. A comparison between the fluorescence spectrum of PP obtained in an argon/AN matrix and the spectrum in neat AN at room temperature. The inset shows the spectrum as recorded in ref 4. The mainframe shows the spectrum obtained by us at 284 nm excitation compared with the red-shifted band extracted from the experimental spectrum.

instance, in the cases of aniline[30] and propylbenzene.[31] The oscillator strength of the X−A transition is very large ∼0.2−0.3.[32] For such allowed transitions, the matrix shift is on the order of 1000 cm^{-1} in argon.[33,34] Because the A state in the gas phase lies about 500 cm^{-1} above the B state, it appears that the emission spectrum observed in the matrix is actually due to the A state and not the B state, in contrast with the case of the isolated molecule.

IVb. PP in AN-Doped Argon Matrixes—Assignment of the Red-Shifted Band. Addition of a small amount of acetonitrile (0.5−2%) leads to the appearance of two distinct bands in the emission spectrum. One is similar in shape and location to the spectrum in neat argon (maximum at 306 nm), and the other is shifted to the red with maximum intensity at about 345 nm. The vibrational structure of the 306 nm band (nicely resolved in an argon matrix, Figure 1) is almost completely washed out, while the 345 band exhibits no vibrational structure. Presumably some PP molecules do not have an immediate acetonitrile neighbor at the low doping ratio used, so the observed spectrum includes also emission from PP molecules surrounded by argon only. (See the discussion of MD simulations herein for support of this contention). At wavelengths longer than 284.1 nm, PP in a neat argon matrix does not absorb, while at least some molecules with an acetonitrile next-neighbor apparently do. Excitation in the 284−295 nm range leads to the emission from the red-shifted band only. The emission maximizes in this case at 350 nm, somewhat red-shifted with respect to the 345 nm peak observed at shorter excitation wavelengths (the 345 nm maximum is thus probably due to spectral overlap of two bands). By comparison, the emission spectrum of PP in liquid acetonitrile at room temperature shows only a small shoulder to the red of the "normal" spectrum.[1,2,4]

The red-shifted band is assigned to a charge-transfer state of PP in the presence of acetonitrile for the following reasons: (1) It is observed in acetonitrile-doped matrixes and not in ethylene doped ones. Acetonitrile is much more polar (dipole moment is 3.9 D) than ethylene, which has no permanent dipole moment. (2) The observed spectrum of PP in liquid acetonitrile was separated in ref 4 into two bands, one of which was assigned to a CT emission. This CT band is red-shifted with respect to the "normal" emission, having maximum intensity at about 360 nm. Figure 6 compares their derived CT emission spectrum with the red-shifted one obtained in the matrix in this work. The striking similarity indicates that the two spectra are due to the same species. (3) The possibility that the band is due to a stable compound photogenerated by a reaction between PP and acetonitrile in an argon matrix is incompatible with the IR experiments designed to detect such species. It might be argued that the IR sensitivity is too low and cannot detect trace amounts. DMABN is chemically similar to PP and would be expected to react in a similar manner. The control experiment with DMABN in which no red-shifted emission was observed is a further support of the proposed assignment.

The nature of the excited states giving rise to the emission spectra in liquid solutions is a matter of some debate, as discussed in the Introduction. It is ordinarily assumed that emission can be observed only from the lowest excited singlet state. In the gas phase, the B state is the lowest excited singlet state of PP and of the "parent" molecule DMABN. However, in a solvent, the order may change because of electrostatic interactions arising from permanent dipoles of the solvent or induced dipoles due to the polarizability of nonpolar solvents. The dipole moments of DMABN and PP in their excited A states are of comparable magnitude (Table 1). Thus, interaction with a polar molecule is expected to downshift the A state potential surface of the two molecules to a similar extent. In DMABN, the separation between the B and A states in the Franck−Condon region is relatively large (∼0.5 eV) compared to only about 0.05 eV in PP (Table 1). Consequently, in a mildly polarizable medium such as a solid argon matrix (polarizability = 1.586 Å^3),[35] the A state can easily become the lowest singlet state of PP, while the B state remains the lowest singlet in the case of DMABN. The presence of the highly polar AN molecule could lead to an observable difference. While in DMABN it takes several nearest neighbors to invert the state ordering, in PP a single AN neighbor might be sufficient. Addition of acetonitrile to the argon matrix apparently does not sufficiently stabilize the CT state in the case of DMABN, so no red-shifted emission is found.

IVc. PP in AN-Doped Argon Matrixes—Excitation Wavelength Dependence of the Spectra. A remarkable result of this work is the excitation wavelength behavior of the emission spectrum in acetonitrile-doped argon matrixes. As the excitation wavelength is shifted to the blue, the intensity of the 345 nm band decreases with respect to that of the 300 nm band. Upon excitation at 270 nm or lower wavelengths, the 345 nm band is hardly observable, and the spectrum is reminiscent of the emission spectrum observed in pure acetonitrile at 300 K.[1,2,4] This kind of wavelength dependence of an emission spectrum in condensed phases is rather unusual.

One trivial explanation is that the absorption cross section of PP neighbored by acetonitrile in an argon matrix is red-shifted with respect to that of PP in pure argon. The observed spectrum is then simply the superposition of two bands: one of PP in argon peaking at 306 nm and the other of PP in argon/acetonitrile host peaking around 350 nm. The observed intensity ratio of the 306 and 345 nm bands varies with the excitation wavelength, according to this interpretation, because it reflects the ratio of the absorption cross sections of the two species as a function of wavelength. However, acetonitrile clearly affects also the 306 nm band, as inferred from the smearing out of the vibrational structure. The 306 nm band is at least partially due to absorption by PP molecules interacting with acetonitrile molecules.

An alternative explanation is the presence of a double well potential surface on the excited state of PP in the polar

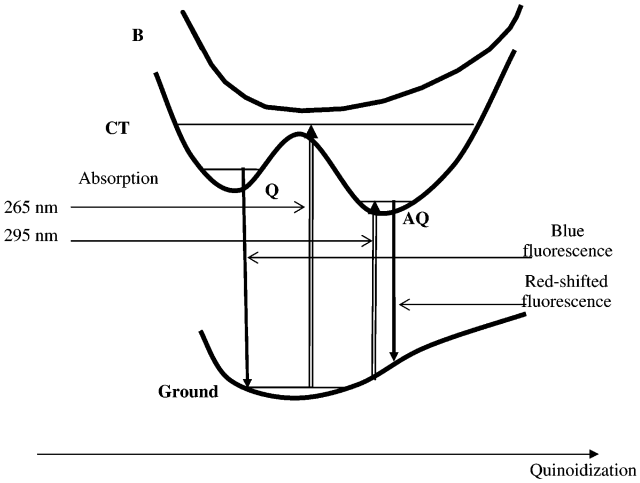


Figure 7. The energy level diagram proposed for PP in an acetonitrile-doped argon matrix. The A state is much more stabilized than the B state because of the large dipole of acetonitrile. The two minima of the charge-transfer A state are more pronounced than those in neat argon. The species lying at the right-hand minimum is more polar than the one lying at the left-hand one. Absorption at long wavelengths leads solely to excitation of the species lying at the right-hand minimum. As the excitation energy increases, both species are excited, leading to dual fluorescence. At the shorter wavelength range (around 265 nm), the absorption leads primarily to the left-hand species.

environment[21] created by the presence of acetonitrile. Figure 7 shows a schematic, one-dimensional depiction of the energy level diagram. As detailed in the Introduction, the A state can support two minima, one in the planar (quinoidal, Q) structure and the other at an antiquinoidal (AQ) form of perpendicular structure. We propose that the right-hand minimum in Figure 7 is due to the AQ form, leading to emission centered around 350 nm. The left-hand minimum is due to the planar Q form, emitting around 300 nm. The close similarity of the spectrum due to the Q form in an acetonitrile-doped argon matrix and the spectrum in neat argon is due to the rather small calculated dipole moment of the Q form (0.7 D).[21]

Another parameter that differentiates PP from DMABN is the fact that the molecule is twisted in the ground state to an intermediate position between the planar geometry and the perpendicular one, while DMABN is essentially planar. The twist angle between the two rings of PP is 38.7° in the ground state.[10] In an argon matrix, the internal rotation to either the planar or the perpendicular forms is restricted. Simple geometric considerations indicate that in many trapping sites there is enough room for the small angle change to take place. We are now running molecular dynamics simulations[26,36] to check this hypothesis more quantitatively. Such detailed MD simulations are also needed to elucidate the factors controlling the fate of the excited PP molecules in sites containing AN molecules. At this time, we note that at high excitation energies the system is biased in favor of molecules emitting from the Q minimum rather than the AQ one. The reasons for this preference are not clear at the moment. A possible speculation is that trapping sites differ in the relative disposition of the AN neighbor with respect to PP, so the absorption cross section for sites favoring the Q minimum at short wavelengths is larger than that of sites leading to the AQ minimum.

IVd. Site Effects. As mentioned in the Introduction, an argon matrix is considered as a rather rigid structure, and large amplitude motions are restricted in it. Therefore, it may be assumed that different trapping sites can result in distinct spectra, giving rise to spectral line splitting. Light absorption may, in principle, result in localized heating that could soften the matrix and allow relaxation of strained molecules. In the present experiments, we believe that the excitation wavelength dependence of the emission spectra offers strong evidence that this is not the case. Softening is expected to allow motion inside the trapping site, allowing the system to reach a global minimum. Softening of the matrix would therefore result in an emission spectrum that is largely independent of the excitation wavelength (as observed in liquid solutions), in contrast with the observation. The fact that different emission spectra are recorded at diverse excitation frequencies indicates that PP occupies distinguishable sites and that they are not exchanged by local heating.

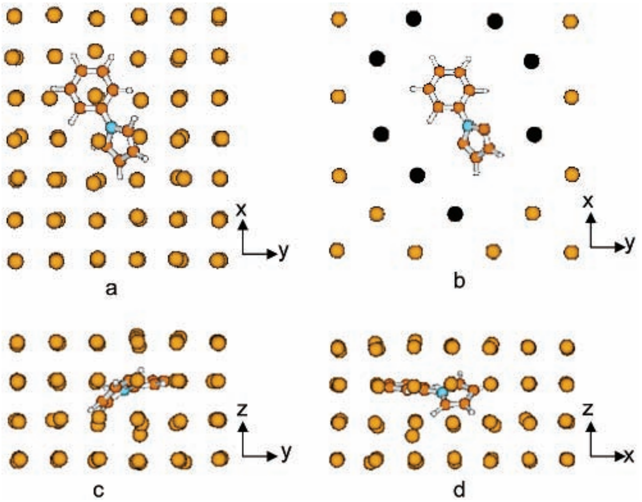


Figure 8. An example of the results of the molecular dynamics calculations, showing the calculated structure of the argon matrix in the vicinity of a six-substitutional trapping site of PP. In this example, five argon atoms are removed from one (100) face and the sixth from an adjacent layer. Several argon atoms are seen to be strongly shifted from their regular position in a neat argon crystal: (a) an overall view along the $x-y$ plane showing the PP molecule and four layers of argon atoms arranged in (100) planes; (b) a view of a single (100) layer from which five argon atoms are replaced by PP (the nearest neighbor atoms, of which the distance from the molecule is less than 4 Å, are shown as black circles); (c) an overall view along the $y-z$ plane showing the PP molecule and four layers of argon atoms arranged in (100) planes; (d) an overall view along the $x-z$ plane showing the PP molecule and four layers of argon atoms arranged in (100) planes.

As any large, asymmetric molecules, PP is expected to occupy several trapping sites in solid argon. We have calculated the structure of the more probable trapping sites using a molecular dynamics simulation program developed in our group;[26,36] a complete report will be published in a forthcoming paper. It turns out that the most stable sites are those in which PP replaces six argon atoms. Several different six-substitutional sites are found; the structure of a frequently encountered one is shown in Figure 8. In this case, each PP molecule has about 20 nearest argon atom neighbors. One acetonitrile molecule typically replaces two argon atoms in the matrix. Therefore, a statistical distribution predicts that each PP molecule has less than one AN nearest neighbor on average when the argon/AN ratio is 100 (as typically used in the experiments). This estimate may fall short of the actual case because dipole−dipole interaction may favor some clustering of PP and AN. Still, it is highly unlikely that a PP molecule will have more than two AN nearest neighbors. It follows that in the argon matrix, only one (or perhaps two) AN molecules suffice to shift the CT state to a lower energy than the B state.

Summary

The emission spectrum of *N*-phenylpyrrole in a neat argon matrix has been recorded for the first time. It is assigned to a highly perturbed A state that strongly interacts with the B state. Addition of the polar molecule acetonitrile leads to the observation of two emission bands the relative intensity of which is strongly excitation wavelength dependent. We propose that both emission bands are due to the charge-transfer A state, which has two distinct minima. The matrix supports different trapping sites that are rigid enough to prevent transitions between the two minima. An interesting result is the fact that (on average) a single acetonitrile neighbor suffices to induce the formation of the red-shifted band of PP, similar to that recorded for PP in acetonitrile solutions.

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