Infrared Spectrum of Nitrobenzene Anion in Solid Argon

Renhu Ma, Dongmei Yuan, Mohua Chen, and Mingfei Zhou*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Advanced Materials Laboratory, Fudan University, Shanghai 200433, P. R. China

Received: September 19, 2008; Revised Manuscript Received: December 9, 2008

The infrared spectrum of the nitrobenzene anion isolated in solid argon is presented. The nitrobenzene anion was prepared by co-deposition of a nitrobenzene/Ar mixture with high-frequency discharged argon at 4 K. Photosensitive absorptions are assigned to different vibrational modes of the nitrobenzene anion on the basis of isotopic substitutions (^{15}N and deuterium), as well as theoretical calculations. The anion loses one electron to give the neutral nitrobenzene upon visible light ($500 < \lambda < 600$ nm) irradiation. Theoretical calculations predicated that the anion has a planar C_{2v} symmetry with a shorter C−N bond and longer N−O bonds relative to those of neutral nitrobenzene.

Introduction

As the simplest nitro-aromatic compound, nitrobenzene is widely used as a precursor molecule for the synthesis of aniline, which is one of the most important aromatic amines in industry. For this reason, the reduction of nitrobenzene has received considerable attention. The reduction processes proceed with the initial formation of a nitrobenzene anion radical, which has been extensively studied.[1−10] The nitrobenzene anion radical has been prepared via the reactions of neutral nitrobenzene with alkaline metals in crystals.[1−3] The infrared spectrum of the crystalline radical anion has been measured.[3] The radical anion has also been produced by electrolytic reduction of nitrobenzene in various salts and solutions, and its electron spin resonance spectra were reported.[4−6] The anion was determined to have a planar structure due to the conjugation of the p orbitals of oxygen atoms with the π electron orbitals of the aromatic ring.

The nitrobenzene anion radical has also been generated in the gas phase. The electron affinity of nitrobenzene was measured by several methods.[7−10] Earlier charge exchange experiments reported a low limit of adiabatic electron affinity to be 0.7 eV.[7] Gas-phase electron transfer equilibrium measurements using a pulsed electron beam high ion source pressure mass spectrometer found the electron affinity of nitrobenzene to be 1.01 eV.[8] A more recent photoelectron spectroscopic study on the nitrobenzene anion yielded an adiabatic electron affinity of 1.00 ± 0.01 eV.[9] The photoelectron spectrum indicates that there is substantial difference in the equilibrium geometries of the anion and neutral forms.

Although the infrared spectrum of the crystalline nitrobenzene anion has been reported, the vibrational spectrum of isolated nitrobenzene anion has not been experimentally characterized. In this paper, we report a matrix isolation infrared absorption spectroscopic study of nitrobenzene anion, which is produced via high-frequency discharge and is isolated in solid argon.

Experimental and Computational Methods

The nitrobenzene anion was prepared by high-frequency discharge in conjunction with matrix isolation. The experimental setup for matrix isolation infrared absorption spectroscopic investigation has been described in detail previously.[11] In the present discharge experiments, the rotating target is replaced by a gas inlet. One pure argon gas stream was subjected to discharge from a high-frequency generator (Tesla coil, alternating voltage ranging from 0 to 9 kV and frequency ranging from 10 to 15 kHz). The tip of the Tesla coil was connected to a copper cap on one end of a quartz tube extending into the vacuum chamber. The other end of the quartz tube was connected to a copper tube with ground potential. Discharge takes place between the cap and the copper tube. The quartz tube is about 20 mm long with an internal diameter of 3 mm. The resulting beam is mixed with another gas stream containing nitrobenzene/Ar sample outside the discharge region, followed by co-deposition on the surface of a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. In general, matrix samples were deposited for 1 h at a rate of approximately 5 mmol/h for each stream. The $C_6H_5NO_2$/Ar mixtures (0.05−0.1% molar ratio) were prepared in a stainless steel vacuum line using a standard manometric technique. $C_6H_5{}^{15}NO_2$ (ISOTEC, 99%) and $C_6D_5NO_2$ (ISOTEC, 99%) were used in different experiments. The $C_6H_5NO_2$ sample was cooled to 77 K using liquid N_2 and was evacuated to remove volatile impurities. The infrared absorption spectra of the resulting samples were recorded on a Bruker Vertex 80v spectrometer at a resolution of 0.5 cm^{-1} between 4000 and 400 cm^{-1} using a DTGS detector. Matrix samples were subjected to broadband irradiation using a tungsten lamp with glass filters.

Quantum chemical calculations were performed using the Gaussian 03 program.[12] The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr (B3LYP) was utilized.[13] The 6-311++G(d,p) basis set was used for all calculations.[14] The geometries were fully optimized, the harmonic vibrational frequencies were calculated, and zero-point vibrational energies (ZPVE) were derived.

Results and Discussion

High frequency discharge is employed in conjunction with the matrix isolation technique to produce and trap the nitrobenzene anion reported here. Experiments were performed with relatively low power of discharge (about 400 V alternating voltage with a frequency of 11 kHz) to optimize the relative

---

* To whom correspondence should be addressed. E-mail: mfzhou@fudan.edu.cn.

10.1021/jp8083293 CCC: $40.75

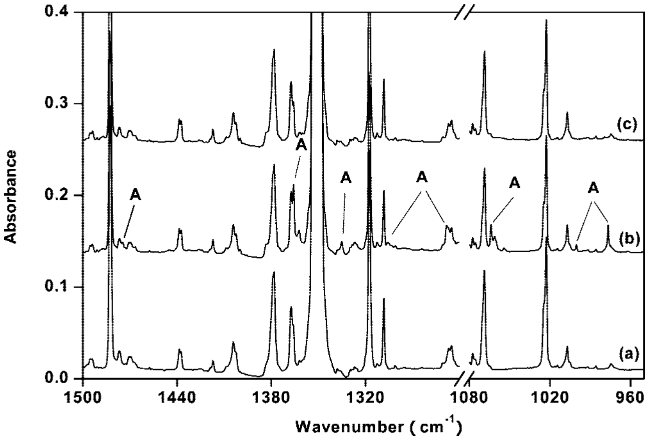

Figure 1. Infrared spectra in the 1500−1280 and 1080−950 cm^{-1} regions of (a) samples from 1 h of 0.1% $C_6H_5NO_2$/Ar deposition at 4 K, (b) samples from 1 h of co-deposition of 0.1% $C_6H_5NO_2$/Ar with high-frequency discharged Ar, and (c) sample from panel b after 15 min of λ > 500 nm irradiation.

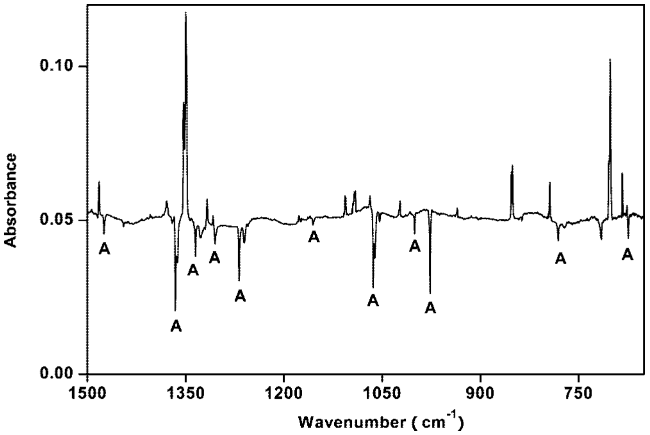

Figure 2. Difference IR spectrum in the 1500−650 cm^{-1} region from co-deposition of 0.1% $C_6H_5NO_2$/Ar with high-frequency discharged Ar at 4 K. Spectrum taken after 15 min of λ > 500 nm irradiation minus spectrum taken right after 1 h of sample deposition; the bands pointing upward are due to neutral nitrobenzene absorptions.

yield of anion absorptions. Condensation of the premixed nitrobenzene/argon gas mixture at 4 K without discharge shows only the nitrobenzene absorptions and trace water and CO_2 impurities. When the nitrobenzene/argon mixture is co-deposited with discharged argon, new absorptions were observed. The infrared spectra in selected regions are shown in Figure 1. After 1 h of sample deposition, absorptions at 1474.7, 1365.7, 1335.0, 1305.4, 1268.6, 1155.6, 1063.8, 1054.4, 1000.3, 976.7, 781.2, and 674.5 cm^{-1} (labeled as "A" in the figures) were observed. These product absorptions can be grouped together (group A hereafter) based on their consistent behavior upon annealing and photolysis. These absorptions remained almost unchanged upon sample annealing to 15−25 K but disappeared when the sample was irradiated by the output of a tungsten lamp with a λ > 500 nm long wavelength pass filter. The difference spectrum shown in Figure 2 (spectrum taken after 15 min of λ > 500 nm irradiation minus spectrum taken right after 1 h of sample deposition) clearly demonstrates that the group A absorptions decreased, while the absorptions of neutral nitrobenzene increased under λ > 500 nm irradiation. Besides the group A absorptions, weak absorptions at 1868.7, 1550.4, 1481.5, and 783.5 cm^{-1} were also observed after sample deposition in the experiments with relatively high power of discharge. These absorptions were previously assigned to the phenoxyl radical−nitric oxide complex.[15] The phenoxyl radical−nitric oxide complex absorptions remained unchanged upon λ > 500 nm irradiation but disappeared upon sample annealing to 25 K, during which another group of absorptions at 1701.5, 1486.3, 1233.8, 764.7, 730.6, and 585.7 cm^{-1} were produced. These absorptions were previously assigned to the phenyl nitrite.[15] In addition, weak HAr_2^+ absorption at 903.4 cm^{-1} was also observed.[16]

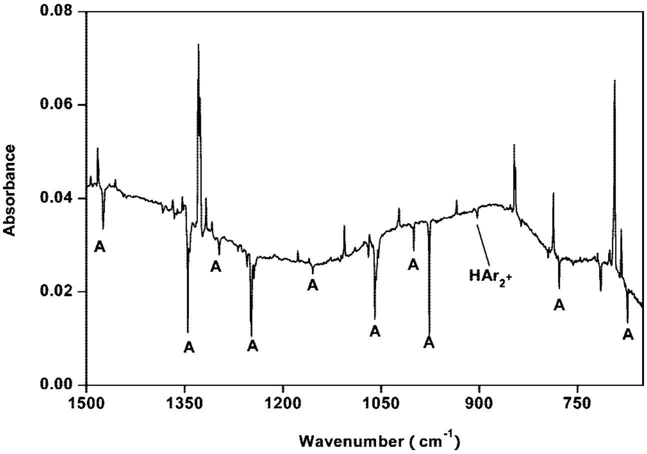

Figure 3. Difference IR spectrum in the 1500−650 cm^{-1} region from co-deposition of 0.1% $C_6H_5{}^{15}NO_2$/Ar with high-frequency discharged Ar at 4 K. Spectrum taken after 15 min of λ > 500 nm irradiation minus spectrum taken right after 1 h of sample deposition; the bands pointing upward are due to ^{15}N-labeled neutral nitrobenzene absorptions.

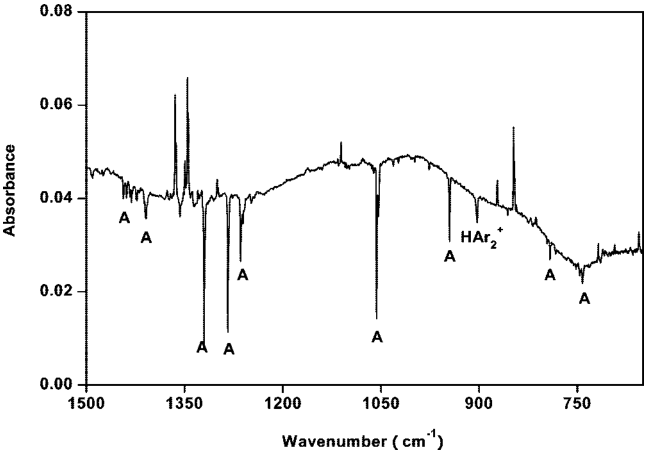

Figure 4. Difference IR spectrum in the 1500−650 cm^{-1} region from co-deposition of 0.1% $C_6D_5NO_2$/Ar with high-frequency discharged Ar at 4 K. Spectrum taken after 15 min of λ > 500 nm irradiation minus spectrum taken right after 1 h of sample deposition; the bands pointing upward are due to deuterium-substituted neutral nitrobenzene absorptions.

Similar experiments were also performed with the isotopically labeled $C_6H_5{}^{15}NO_2$ and $C_6D_5NO_2$ samples. The difference spectra in selected regions with the $C_6H_5{}^{15}NO_2$ and $C_6D_5NO_2$ samples are shown in Figures 3 and 4, respectively. The band positions of group A absorptions and their isotopic counterparts are listed in Table 1.

Co-deposition of nitrobenzene with high-frequency discharged argon led to the appearance of group A absorptions, which are favored in the experiments with relatively low power of discharge. Our recent experiments show that the charged species become obvious when relatively low power of discharge was employed.[17] These absorptions are destroyed under visible light

TABLE 1: Comparison between the Calculated and Observed Vibrational Frequencies and Intensities for the Nitrobenzene Anion ($C_6H_5NO_2^-$)

	calcd frequency (intensity)[a]			exptl frequency (intensity)[b]		
	$C_6H_5NO_2^-$	$C_6H_5{}^{15}NO_2^-$	$C_6D_5NO_2^-$	$C_6H_5NO_2^-$	$C_6H_5{}^{15}NO_2^-$	$C_6D_5NO_2^-$
a_1	3211.8 (1)	3211.8 (1)	2374.5 (2)			
b_2	3210.5 (6)	3210.5 (6)	2371.6 (3)			
a_1	3162.5 (47)	3162.5 (47)	2339.6 (13)			
b_2	3131.4 (66)	3131.4 (66)	2311.4 (34)			
a_1	3124. 9 (7)	3124.9 (7)	2302.2 (6)			
a_1	1614.9 (90)	1614.5(94)	1578.7 (89)	1474.7 (0.19)	1474.3 (0.31)	1443.4 (0.14)
b_2	1550.9 (1)	1550.2 (2)	1514.6 (0)			
a_1	1493.0 (3)	1491.2 (0)	1300.9 (142)			1283.8 (0.90)
b_2	1472.9 (4)	1471.5 (2)	1383.8 (4)			
a_1	1373.2 (232)	1349.8 (209)	1416.3 (124)	1365.7 (1.00)	1345.2 (1.00)	1408.7 (0.24)
b_2	1365.8 (118)	1361.6 (67)	1355.9 (177)	1335.0 (0.21)		1320.2 (1.00)
b_2	1333.6 (66)	1324.2 (37)	1040.9 (2)	1305.4 (0.10)	1297.3 (0.18)	
b_2	1296.6 (103)	1281.2 (174)	1290.9 (119)	1268.6 (0.43)	1247.9 (0.80)	1264.4 (0.49)
a_1	1176.3 (7)	1175.4 (7)	866.1 (8)	1155.6 (0.06)	1154.4 (0.07)	
b_2	1155.3 (4)	1155.3 (4)	838.5 (0)			
a_1	1087.1 (193)	1083.9 (204)	1074.4 (204)	1063.8 (0.85)	1059.6 (0.80)	1056.7 (0.96)
b_2	1076.7 (18)	1076.5 (19)	811.8 (7)	1054.4 (0.07)	1054.4 (0.17)	
a_1	1017.0 (36)	1017.0 (36)	810.0 (8)	1000.3 (0.15)	1000.3 (0.18)	792.0 (0.07)
a_1	990.7 (77)	990.5 (75)	956.8 (48)	976.7 (0.80)	976.7 (0.78)	945.3 (0.41)
a_2	943.4 (0)	943.4 (0)	757.2 (0)			
b_1	926.9 (1)	926.9 (1)	737.7 (2)			
b_1	820.2 (16)	820.1 (16)	680.0 (7)			
a_2	807.5 (0)	807.5 (0)	628.4 (0)			
a_1	794.6 (30)	792.2 (26)	758.5 (29)	781.2 (0.13)	778.1 (0.19)	742.4 (0.07)
b_1	695.5 (85)	695.3 (86)	533.2 (9)	674.5 (0.14)	674.0 (0.19)	
a_1	655.1 (0)	653.8 (0)	639.1 (0)			
b_1	650.0 (4)	649.7 (4)	598.6 (0)			
b_2	628.0 (0)	628.0 (0)	600.9 (0)			
b_1	529.2 (26)	520.1 (26)	495.0 (63)			
b_2	522.6 (3)	520.5 (3)	507.4 (3)			
a_2	435.1 (0)	435.1 (0)	383.8 (0)			
a_1	402.8 (10)	401.7 (9)	394.5 (10)			
b_1	381.6 (0)	378.2 (0)	347.1 (1)			
b_2	248.7 (1)	248.7 (1)	238.4 (1)			
b_1	157.5 (2)	157.5 (2)	148.0 (2)			
a_2	110.1 (10)	110.1 (0)	106.8 (0)			

[a] In km/mol. [b] Integrated intensity normalized to the most intense absorption.

(λ > 500 nm) irradiation, which suggests that the group A absorptions are due to an anion species. The difference spectrum in Figure 2 clearly demonstrates that the group A absorptions were converted to the neutral nitrobenzene absorptions upon visible light irradiation. These experimental observations lead to the assignment of group A absorptions to different vibrational modes of the nitrobenzene anion radical, as listed in Table 1.

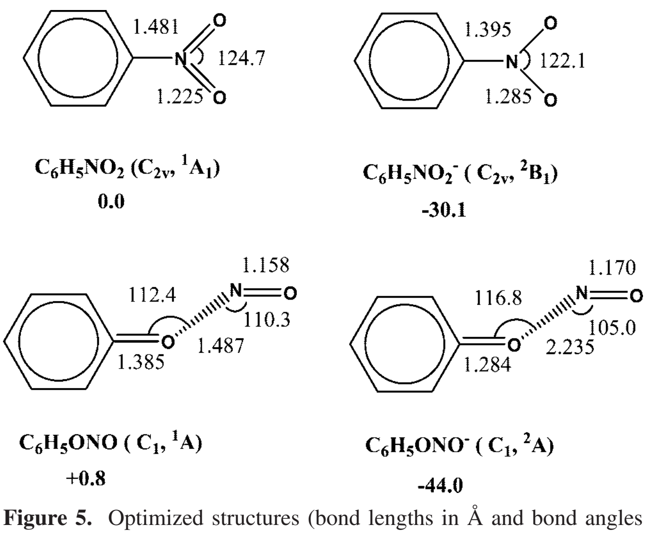

Figure 5. Optimized structures (bond lengths in Å and bond angles in deg) and relative stabilities (kcal/mol) of $C_6N_5NO_2$, C_6H_5ONO, $C_6H_5NO_2^-$, and $C_6H_5ONO^-$.

Density functional calculations at the B3LYP/6-311++G** level of theory predicted that the nitrobenzene anion ($C_6H_5NO_2^-$) has a $^2B_1$ ground state with a planar C_{2v} symmetry (Figure 5), in agreement with previous reports.[5−9] The neutral nitrobenzene, which was calculated to have the same symmetry as nitrobenzene anion is also shown in Figure 5 for comparison. The $^2B_1$ state is the only state that lies lower in energy than the ground state of neutral nitrobenzene. The first excited state of the anion was predicted to be 36.6 kcal/mol above the $^2B_1$ ground state. The calculation results show that the C−N bond length of the anion is about 0.086 Å shorter than that of the neutral, while the N−O bond is 0.06 Å longer than that of the neutral. As shown in Figure 6, the lowest unoccupied molecular orbital (LUMO) of neutral nitrobenzene is a π orbital, which consists of the antibonding π orbital of the NO_2 fragment and the π orbital of the aromatic ring. Adding one electron to this orbital results in the $^2B_1$ ground-state anion. Because the LUMO of the neutral species is C−N bonding but N−O antibonding in character, an electron added in this orbital elongates the N−O bond and shortens the C−N bond. The 3D contour of the singly occupied molecular orbital of the nitrobenzene anion is about the same as that of the LUMO of neutral nitrobenzene.

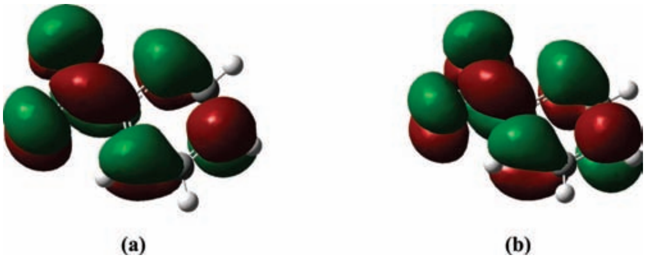

Figure 6. The 3D contours of (a) the lowest unoccupied molecular orbital of neutral nitrobenzene and (b) the singly occupied molecular orbital of nitrobenzene anion.

The absorptions are assigned based on comparison to the absorptions of the neutral $C_6H_5NO_2$ molecule as well as density functional frequency calculations. The calculated vibrational frequencies and intensities are compared with the experimental values in Table 1. The strongest absorption of group A is located at 1365.7 cm^{-1}, which shifted to 1345.2 cm^{-1} with $C_6H_5{}^{15}NO_2$. The band position and isotopic shifts indicate that this absorption can be attributed to a CN stretch vibration (a_1). The corresponding mode of neutral nitrobenzene is observed at 1353.4 cm^{-1}, ca. 12.3 cm^{-1} lower than that of the anion. As has been discussed above, when one electron is added to the neutral nitrobenzene in forming the anion, the CN bond is shortened, which is consistent with the observed blue shift of the CN stretch vibration of the anion with respect to the neutral. This mode also was theoretically predicted to be the strongest absorption of the anion at 1373.2 cm^{-1} (Table 1) with a nitrogen isotopic shift of 23.4 cm^{-1}. For $C_6D_5NO_2{}^-$, there are two a_1 symmetry modes for the CN stretch vibration predicted at 1416.3 and 1300.9 cm^{-1} that have appreciable IR intensities. Both modes were experimentally observed at 1408.7 and 1283.8 cm^{-1} (Table 1). The 1063.8 cm^{-1} absorption is the second strongest band. This absorption exhibits small ^{15}N (4.2 cm^{-1}) and deuterium (7.1 cm^{-1}) isotopic shifts, suggesting that the mode is largely due to C or O motions, and therefore is assigned to the NO stretch and CC bending mixed mode (a_1). The corresponding mode of the neutral nitrobenzene is observed at 1106.8 cm^{-1} in solid argon with a relatively small ^{15}N shift of 1.0 cm^{-1}. This mode of the anion was theoretically predicted at 1087.1 cm^{-1} with a slightly smaller ^{15}N shift of 3.2 cm^{-1}. The 1268.6 cm^{-1} absorption is slightly weaker than the above-mentioned absorptions. This absorption exhibits a quite large ^{15}N shift of 20.5 cm^{-1}. The band position and isotopic shift are suggestive of an antisymmetric NO stretch vibration. As a reference point, the antisymmetric N−O stretch mode of the $NO_2{}^-$ anion is observed at 1244 cm^{-1} in solid argon.[18] The antisymmetric NO stretch mode of nitrobenzene is located at 1544.1 cm^{-1} in solid argon, which is 275.5 cm^{-1} higher than the anion absorptions. The large red shift of this vibrational mode from neutral to anion species is due to the weakening of the N−O bonds when an electron is added to the LUMO of neutral nitrobenzene to give the anion. The weak 1335.0 cm^{-1} absorption is due to a CC stretch mode (b_2). This mode shifted to 1320.2 cm^{-1} and becomes one of the most intense absorptions in the spectrum with the $C_6D_5NO_2$ sample. This mode is theoretically predicted at 1365.8 cm^{-1} with a deuterium shift of 9.9 cm^{-1}, very close to the observed shift of 14.8 cm^{-1}. The calculations also predicted that this mode is intensified with deuterium substitution. The 1474.7 cm^{-1} absorption shows small ^{15}N and deuterium isotopic shifts and is assigned to the CC stretch mode (a_1). The even weaker absorption at 1305.4 cm^{-1} shows an ^{15}N shift of 8.1 cm^{-1} and is a NO stretch and CH bending mixed mode (b_2). In the low-frequency region, the 781.2 cm^{-1} absorption shows a small ^{15}N shift (3.1 cm^{-1}). This absorption is assigned to a mixed mode of ONO bending and chair deformation (a_1).

Besides the above-mentioned vibrations, all the other absorptions experimentally observed show very smalll ^{15}N shift, suggesting that these absorptions are due to aromatic ring vibrations. Among these, the 976.7 cm^{-1} absorption is the strongest one and is assigned to the CC bending mode of the anion (a_1). DFT calculations gave a value of 990.7 cm^{-1} with 0.2 cm^{-1} ^{15}N shift and a 33.9 cm^{-1} deuterium shift, which are in good agreement with the experimental observations. The very weak 1155.6, 1054.4, and 1000.3 cm^{-1} absorptions are attributed to ring breathing or CH bending vibrations. The 674.5 cm^{-1} absorption is the most intense absorption in the low-frequency region. It is assigned to a mixed mode of chair deformation and CH bending.

Besides the above-mentioned group A absorptions, an absorption at 715.2 cm^{-1} decreased together with group A absorptions on photolysis (Figure 2) with an ^{15}N counterpart at 714.6 cm^{-1}. This absorption cannot be assigned.

As can be seen in Table 1, the calculated harmonic gas-phase vibrational frequencies are higher than the experimentally observed values. Because vibrational frequencies tend to be red-shifted by argon matrix relative to those in the gas phase,[19] the calculated frequencies are in good agreement with the experimental values after taking the anharmonic and matrix effect into consideration. However, the predicted relative IR intensities do not match the experimental observations as well as the frequencies. Some CH stretch modes were calculated to have appreciable IR intensities. However, these modes were not observed in the experiments. As has been reported, DFT calculations tend to overestimate some vibrations such as CH stretch vibrations.[20,21]

The nitrobenzene anion has previously been prepared by reacting alkaline metal atoms with neutral nitrobenzene.[1−3] The infrared absorption spectrum of crystalline nitrobenzene anion has been reported. The most intense absorption of the crystalline anion is the antisymmetric NO stretch mode reported at 1220 cm^{-1}, which is lower than the corresponding mode of the anion isolated in solid argon. The anion in the crystal is coordinated by a Na^+ counterion. Because the negative charge of the nitrobenzene anion is largely located on the two oxygen atoms, the Na^+ ion should be coordinated to the oxygen atoms of nitrobenzene anion, which results in a reduction of the N−O stretch frequency. We also calculated the $(C_6H_5NO_2{}^-)(Na^+)$ complex, which we found to have a planar C_{2v} structure with the Na^+ ion coordinated to the oxygen atoms. The antisymmetric NO stretch mode was predicted at 1236.9 cm^{-1}. Population analysis shows that the natural charge of the nitrobenzene fragment is −0.72e. Therefore, the Na^+-coordinated nitrobenzene anion should be regarded as a partially charged $(C_6H_5NO_2)^{-0.72}$ anion.

The nitrobenzene anion is formed by electron capture of the neutral species during the co-condensation process, which is an exothermic reaction. The present DFT calculations predicted that the electron affinity of nitrobenzene is about 1.3 eV, slightly higher than the experimentally determined value of 1.0 eV.[9] In the present study, the nitrobenzene anion absorptions disappeared upon $\lambda > 500$ nm irradiation, while the neutral nitrobenzene absorptions increased about 5%. The experiment shows that only the photons in the 500−600 nm (2.06−2.48 eV) wavelength range are responsible for the electron detachment. The photon energy required for electron detachment of nitrobenzene anion in solid argon is about twice as large as the electron affinity of nitrobenzene in the gas phase.

Recent investigations in this laboratory have shown that nitrobenzene is able to be rearranged to phenyl nitrite upon UV light irradiation.[15] Phenyl nitrite is a structural isomer of nitrobenzene, which is only slightly less stable than nitrobenzene. Both phenyl nitrite and its decomposition product phenoxyl radical−nitric oxide complex were observed in the present experiments when relatively high power of discharge was used. Geometry optimization on the phenyl nitrite anion converged to a phenoxyl anion−nitric oxide complex (Figure 5), which is 13.9 kcal/mol lower in energy than the nitrobenzene anion isomer. However, no evidence was found for the formation of phenoxyl anion or phenoxyl anion−nitric oxide complex in the present experiments. The isomerization reaction from the nitrobenzene anion to the phenoxyl anion−nitric oxide complex was predicted to proceed via a transition state that lies about 65.3 kcal/mol above the nitrobenzene anion.

Conclusions

The nitrobenzene anion has been produced by co-deposition of the neutral nitrobenzene with high-frequency discharged Ar at 4 K. The infrared spectra of $C_6H_5NO_2^-$ and isotopically substituted $C_6H_5{}^{15}NO_2^-$ and $C_6D_5NO_2^-$ anions isolated in solid argon were measured. Photosensitive absorptions were assigned to different vibrational modes of the nitrobenzene anion on the basis of deuterium and ^{15}N shifts and theoretical frequency calculations. Density functional calculations predicted that the nitrobenzene anion has a planar C_{2v} structure with a shorter C−N bond and longer N−O bonds compared with those of neutral nitrobenzene, which results in a red shift of the N−O stretch vibration. The anion detaches one electron in forming the neutral nitrobenzene upon visible light ($500 < \lambda < 600$ nm) irradiation in solid argon.

Acknowledgment. This work is supported by NKBRSF (Grant 2007CB815203) and NNSFC (Grant 20773030) of China.

References and Notes

(1) Russell, G.; Bemis, A. *Inorg. Chem.* **1967**, *6*, 403.

(2) Gross, J.; Barnes, J.; Brown, J. *J. Appl. Chem.* **1970**, *20*, 162.

(3) Baronetskii, A. O.; Kuzyants, G. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1980**, *29*, 1267.

(4) Geske, D. H.; Maki, A. H. *J. Am. Chem. Soc.* **1960**, *82*, 2671.

(5) Swartz, G. L.; Gulick, W. M., Jr. *Mol. Phys.* **1975**, *30*, 869.

(6) Mason, R. P.; Harriman, J. E. *J. Chem. Phys.* **1976**, *65*, 2274.

(7) Lifshitz, C.; Tiernan, T. O.; Hughes, B. M. *J. Chem. Phys.* **1973**, *59*, 3182.

(8) (a) Grimsrud, E. P.; Chowdury, S.; Kerbale, P. *J. Chem. Phys.* **1985**, *83*, 1095. (b) Grimsrud, E. P.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 4627.

(9) Desfrancois, C.; Periquet, V.; Lyapustina, S. A.; Lippa, T. P.; Robinson, D. W.; Bowen, K. H.; Nonaka, H.; Compton, R. N. *J. Chem. Phys.* **1999**, *111*, 4569.

(10) Modelli, A.; Venuti, M. *Int. J. Mass Spectrom.* **2001**, *205*, 7.

(11) Wang, G. J.; Zhou, M. F. *Int. Rev. Phys. Chem.* **2008**, *27*, 1.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(14) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(15) Yang, R. J.; Jin, X.; Wang, W. N.; Fan, K. N.; Zhou, M. F. *J. Phys. Chem. A* **2005**, *109*, 4261.

(16) (a) Bondybey, V. E.; Pimentel, G. C. *J. Chem. Phys.* **1972**, *56*, 3832. (b) Milligan, D. E.; Jacox, M. E. *J. Mol. Spectrosc.* **1973**, *46*, 460. (c) Wight, C. A.; Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *65*, 1244.

(17) (a) Yu, L.; Zeng, A. H.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 8264. (b) Zeng, A. H.; Yu, L.; Wang, Y.; Kong, Q. Y.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 6656. (c) Zhou, H.; Gong, Y.; Zhou, M. F. *J. Phys. Chem. A* **2007**, *111*, 603.

(18) Milligan, D. E.; Jacox, M. E.; Guillory, W. A. *J. Chem. Phys.* **1970**, *52*, 3864.

(19) Jacox, M. E. *Chem. Soc. Rev.* **2002**, *31*, 108.

(20) Lee, Y. K.; Manceron, L.; Papai, I. *J. Phys. Chem. A* **1997**, *101*, 9650.

(21) Miao, L.; Dong, J.; Yu, L.; Zhou, M. F. *J. Phys. Chem. A* **2003**, *107*, 1935.

JP8083293