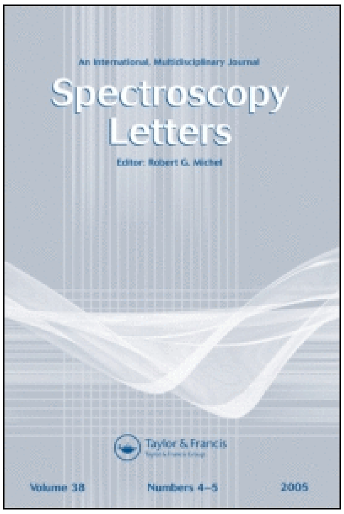

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Phase Dependence of the IR Spectra of Nitrobenzene

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PHASE DEPENDENCE OF THE IR SPECTRA OF NITROBENZENE

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Abstract

The IR spectra of nitrobenzene-d_0 and $-d_5$ were recorded in gas and liquid phases at 25° C and in amorphous solid phase at -170°C. The appearance of new bands and intensity changes going from liquid to solid phase spectrum, are interpreted in terms of molecular symmetry modifications. A normal coordinates analysis was performed and the potential energy distribution agrees well with previous assigments.

Introduction

A significant ammount of work have been done on the vibrational analysis of monosubstituted benzene derivatives (1). Among these, nitrobenzene and its isotopomers have received special attention (2-6). Since the pionnering work of Randle and Whiffen (2), which concerned just the stretching of the nitro group, the understanding about the normal modes of vibrations of this kind of structure has increased enormously. Even though the most recent works proposed a complete assignment of the experimental frequencies, some of them were tentatively assigned

(5,6). Despite this fact, no attention has been paid to the IR spectrum of nitrobenzene in amorphous solid phase.

In the present work we have reexamined the IR spectrum of nitrobenzene and its perdeutero derivative in the gas and liquid phases, and obtained for the first time the amorphous solid spectrum. Interesting experimental observations, particularly comparing the liquid and amorphous solid spectra, are interpreted as a consequence of lowering the molecular symmetry point group of nitrobenzene. We performed a normal coordinates calculation that reproduces the experimental frequencies of nitrobenzene-d_0 and -d_5. With the generated force field we have also calculated the frequencies of nitrobenzene-p-d_1.

Experimental Section

Nitrobenzene-d_0 and -d_5 were obtained from commercial sources (Aldrich and Stholer respectively) at the highest purity available (99 + % and 99.5 % respectively) and used without further purification. Spectra were obtained using a Perkin Elmer 621 IR spectrophotometer and the frequencies measured with an uncertainty of ± 2 cm^{-1}. Amorphous solid spectra were recorded from 600 to 4000 cm^{-1} at liquid air temperature, immediately after freezing the sample in a vacuum cell designed for this purpose. Liquid phase spectra were recorded at room temperature using thin films. Gaseous samples, also measured at room temperature, were prepared in standar 10 cm gaseous sample cells.

The normal coordinates calculations were performed on a microcomputer Zenith Z-200 equipped with a 80287 co-processor, using a set of programs some transferred from mainframe computers.

Results and Discussion

Nitrobenzene is a planar molecule that belongs to the C_{2v} point symmetry group. It has 14 atoms and 36 fundamental frequencies, which are distributed as follows: 13 A_1, 4 A_2, 7 B_1 and 12 B_2. Previous assignments, some aided with Raman polarization measurements, to the different irreducible representations have been already proposed (5,6).

Fig. 1 shows the IR spectrum of nitrobenzene in liquid and amorphous solid phases from 600 to 1700 cm^{-1}. An inspection to this figure reveals drastic changes in the relative intensities of some of the bands between both spectra. A more careful analysis shows that, in many cases, the relative intensity of the totally symmetric A_1-vibrations increase going from the liquid to the amorphous solid spectrum. On the other hand, some of the totally asymetric B_2-vibrations decrease considerably in relative intensity. Perhaps the most interesting experimental observation is the appearance of two new bands in the frozen sample spectrum, at 965 and 830 cm^{-1}, which were not present in the liquid spectrum. Also from fig. 1 can be observed that a number of low intensity new bands appeared in the amorphous solid. These are atributed to overtone and combination bands.

The present experimental observations can be understood in terms of a decrease in the molecular symmetry of nitrobenzene. The average molecular geometry, in gas or liquid phase, more likely correspond to a planar C_{2v} structure. With this geometry, the totally symmetric A_1 vibrations do not contribute significantly to change the molecular dipole moment, however the totally asymmetric B_2 vibrations have a more important contribution. In the amorphous solid the molecule is not planar, the nitro group remains out of the aromatic ring plane and the

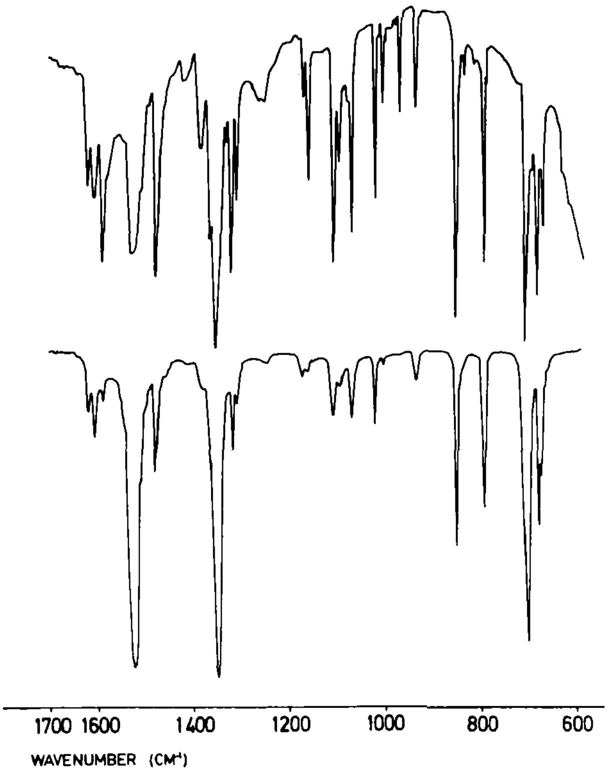

Fig. 1 Infrared spectra of nitrobenzene-d_0 in amorphous solid phase (top spectrum) and liquid phase (bottom spectrum)

molecule now belongs to the C_2 point symmetry group. In this conformation, the contribution from the totally symmetric vibrations to change the molecular dipole moment become more important, and the contribution from the asymmetric ones is not as important as before. This phenomenon is well illustrated by the bands at 1588 and 1525 cm^{-1}, which belong to the A_1 and B_2 representations respectively. The band at 1588 cm^{-1}, according to previous assignments and our potential energy distribution

TABLE 1

Observed and calculated frequencies of nitrobenzene-d_o and calculated potential energy distribution (PED). Symbols: st □ stestreching; bn = bending, op = out of plane bending; tr= torsion.

	Obs Freq (cm^{-1})	Calc.Freq. (cm^{-1})	PED (%)*
A_1	3118	3120	CH st(100)
	3085	3086	CH st(100)
	3035	3045	CH st(100)
	1588	1591	CC st(46),CCH bn(20),CCC bn(12)
	1478	1487	CC st(29),CN st(29),CCH bn(18)
	1348	1356	NO_2 st(37),CN st(18),CCH bn(13)
	1158	1163	CCH bn(61),CC st(31),CCH bn(16)
	1108	1112	CCH bn(63),CC st(11)
	1092	1095	CCC bn(42),NO_2 st(24)
	1004	1006	CC st(57),CCC bn(40)
	852	854	NO_2 st(25) bn(24),CC st(24)
	682	675	CCC bn(40),NO_2 bn(35),CC st(20)
	395	395	CCC bn(68),CN st(21)
A_2	965	969	CH op(100)
	830	819	CH op(100)
	394	398	CCCC tr(80),CH op(11)
	70(*)	69	NO_2 tr(76),CCCC tr(22)
B_1	1018	1014	CH op(78),CCCC tr(13)
	935	932	CH op(52),CCCC tr(21),NO_2 tr(18)
	792	789	CH op(45),CCCC tr(44)
	706	703	NO_2 op(45),NO_2 tr(25),CCCC tr(16)
	672	670	CCCC tr(62),NO_2 op(25)
	420	436	CH op(37),CCCC tr(29),NO_2 tr(25)
	176(*)	185	NO_2 tr(37),CCCC tr(23),CH op(20)
B_2	3118	3119	CH st(100)
	3085	3089	CH st(100)
	1608	1618	CC st(35),CCH bn(23)
	1525	1535	NO_2 st(30),CC st(30),CNO bn(16)
	1364	1373	CC st(65),CCH bn(15)
	1318	1326	NO_2 st(40),CC st(40)
	1308	1315	CCH bn(82)
	1168	1170	CCH bn(87)
	1088	1074	CCH bn(68),CC st(15)
	615	615	CNO bn(52)
	530	535	CCC bn(59),CC st(20)
	254(*)	253	CCN bn(54),CNO bn(28)

(*) Frequencies taken from ref. (8)

\# Contributions smaller than 10% are not included calculation (PED, see Table 1), corresponds to one of the in plane C=C stretching vibrations. In the planar average structure, the contribution from this motion to change the molecular dipole moment is small. After freezing the sample this contribution become more important, since the aromatic ring and the nitro group are not in the same plane. Consequently the relative intensity of this band increases going from the liquid to the solid spectrum. The band at 1525 cm^{-1} belongs to the totally asymmetric B_2-representation and according to previous assignments and our PED calculation, corresponds to the asymmetric NO_2 stretching vibration. In the planar configuration the contribution from this mode to change the molecular dipole moment is important and the band is intense. However, in the solid state this contribution become less important and consequently the intensity of the band decreases. The apearence of two new bands in the solid at 968 and 830 cm^{-1}, can also be explained on the same basis. Under the C_{2v} point group the A_2 modes are IR inactives, by lowering the symmetry to C_2 they become IR active modes. Unfortunately, we were not able to record the amorphous solid spectrum below 600 cm^{-1} and could not detect the remaining A_2 band, at 393 cm^{-1} in the Raman Spectrum (5).

We have performed a force field calculation using a self-consistent iterative procedure based on Wilson´s GF -matrix method (8). In order to calculate the molecular force field the user must provide vibrational frequencies of the molecule and one isotopic derivative. More details about the iterative procedure can be found in the literature (9,10). The final transferable force field is obtained from the average of the force fields generated for the molecule and the isotopomer.

TABLE 2

Observed and calculated frequencies of nitrobenzene-d_5 and -d_1. Experimental frequencies of nitrobenzene-p-d_1 were taken from ref. (6).

	C_6D_5-NO_2			C_6H_4D-p-NO_2	
	Obs Freq (cm^{-1})	Calc Freq (cm^{-1})		Obs Freq (cm^{-1})	Calc Freq (cm^{-1})
A_1	2318	2317	A_1	3077	3055
	2290	2289		3077	3052
	2278	2271		2300	2286
	1540	1537		1586	1587
	1465	1457		1471	1485
	1340	1332		1345	1356
	1075	1072		1175	1160
	960	958		1108	1111
	870	868		1018	1095
	842	839		987	987
	809	807		851	853
	652	659		676	668
	395	385		393	392
A_2	786	782	A_2#	965	969
	630	638		830	819
	353	350		394	398
	66(*)	67		70	69
B_1	842	845	B_1	966	1014
	840	838		878	932
	718	721		761	789
	615	617		690	703
	542	544		606	669
	390	377		421	436
	166(*)	159		170	184
B_2	2305	2304	B_2	3077	3119
	2290	2287		3077	3088
	1589	1579		1604	1590
	1518	1509		1521	1517
	1358	1350		1416	1370
	1305	1297		1316	1326
	1040	1035		1300	1239
	852	851		1108	1093
	812	807		878	918
	590	590		608	611
	508	504		528	534
	242(*)	243		-	252

(*) Frequencies from ref. (6)

(#) The same frequencies that nitrobenzene-d_0 are assumed

A set of suitable symmetry coordinates for nitrobenzene were constructed and the iterative process mentioned before was carried out on nitrobenzene-d_0 and -d_5. For the purpose of the calculation we adopted a planar structure with the following geometrical parameters: r_{CC}= 139.7 pm, r_{CN}= 148.6 pm, r_{CH}= 108.4 pm, r_{NO}= 120.8 pm (7), and all the Euler angles were considered ideal, 120°. The calculated and experimental frequencies as well as the potential energy distribution are shown in Table 1. An examination of the PED on this table reveals a close agreement between previous assignments and the calculated character of the modes, even though these are considerably mixed. Table 2 shows the calculated and experimental frequencies of nitrobenzene-d_5, and the predicted frequencies of nitrobenzene-d_1 together with the experimental values from reference (5). The frequencies of nitrobenzene-do and d_5 are reproduced with 0.8% average deviation, however the predicted values for nitrobenzene-p-d reflect a much larger error (2,4% average deviation). This difference could arise from discrepancies on the assignments of the experimental frequencies.

Finally, we would like to emphasize the fact that, in some instances, more information about molecular structure can be obtained by comparision of IR spectra of liquid and amorphous solid phases.

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