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Dispersed Fluorescence Spectra and ab Initio Calculations of *o*-Cyanophenol

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The vibronic spectrum of *o*-cyanophenol has been measured up to 2000 cm^{-1} above the electronic origin at 33954 cm^{-1} with laser-induced fluorescence spectroscopy. The electronic ground-state frequencies were determined using dispersed fluorescence spectroscopy and the assignment was supported by ab initio calculations on the MP2 level and DFT calculations using B3LYP. Additional CASSCF calculations have been carried out for theoretical description of the S$_1$ state.

1. Introduction

Laser spectroscopy in supersonic jets is a well established method to investigate species which are usually not stable, e.g., hydrogen bonded clusters or radicals[1−7] and references therein. Beyond that, the adiabatic expansion cools rotational and vibrational degrees of freedom resulting in much simpler spectra. In the case of (aromatic) molecules with hydroxyl groups, the hindered rotation of the OH group is cooled and different minimum energy structures (rotamers) can exist simultaneously.

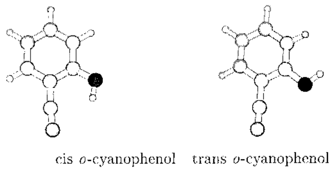
As for *o*-cyanophenol, there are two possible forms: one with the hydroxyl group pointing toward the cyano group and another with the hydroxyl group pointing away from it, cf. Figure 1. In the following we refer to these species as cis and trans rotamers, respectively.

We investigated the vibrations in the first electronically excited state by means of laser-induced fluorescence excitation spectroscopy. Dispersion of the fluorescence from excitation of different vibronic levels was used to determine the ground-state frequencies. The isomer selectivity of this method should be useable to distinguish between the two possible rotamers. Comparison with ab initio calculated frequencies supports the assignment.

2. Experimental Section

The experimental setup has already been described in detail.[8,9] In brief, the sample was expanded through a pulsed nozzle (500 μm orifice) in a vacuum chamber using Helium as carrier gas. The output of an excimer (LPX 100) pumped Dye-laser (FL2002, both Lambda-Physics) was frequency doubled and crossed perpendicularly with the molecular beam. The fluorescence was collected and focused perpendicularly to laser and jet and dispersed by an 1 m monochromator (Jobin Yvon) using a grating with 2400 grooves/mm. The dispersed fluorescence was recorded with an intensified CCD camera. A single fluorescence spectrum was obtained by summing the fluorescence of 200 laser pulses and subtracting the scattered light background (gas pulse off) after 200 laser pulses. The spectra shown here result from an averaging of 50−100 single spectra.

o-Cyanophenol (Fluka) was used without further purification. The sample was heated to about 80 °C to get a sufficent concentration of *o*-cyanophenol in the jet.



cis *o*-cyanophenol trans *o*-cyanophenol

Figure 1. The two rotamers of *o*-cyanophenol.

3. Theoretical Methods and Results

Ab initio calculations at the MøllerPlesset (MP2, frozen core), Density Functional Theory (DFT) and Complete Active Space Self-Consistent Field (CASSCF) level of theory have been carried out using GAUSSIAN[10] for the CASPT2 calculations we used MOLCAS.[11] All structures have been fully optimized with 1×10^{-8} hartree as SCF convergence criterion and 1.5×10^{-5} hartree/bohr and hartree/degree, respectively, as convergence criterion for the gradient optimization of the structures. We used Pople's basis set 6-31G(d,p) for the CASSCF calculations and the 6-311G(d,p) basis set for the MP2 and DFT calculations. The functional used was the B3LYP hybrid provided by the program.

We restricted the molecular geometry to be planar both in the electronic ground and first electronically excited state. The vibrational frequencies were obtained by performing a normal-mode analysis based on the optimized geometries using analytical gradients of the energy. The CASSCF calculations have been carried out in a 10 electrons in 9 orbitals active space covering the π orbitals of the aromatic ring and the cyano group and the nonbonding orbital of the oxygen atom of a'' symmetry.

3.1. Stabilization and Excitation Energy. According to the calculations, *cis*-*o*-cyanophenol turns out to be 767 cm^{-1} more stable in the electronic ground state than the trans isomer on the MP2 level and 891 cm^{-1} with B3LYP. This can be traced back to a weak intramolecular hydrogen bond with the OH group pointing toward the CN group. Note that in the ground state the C−C−N angle of the cis isomer (MP2 175.9 °, B3LYP 176.3 °) is slightly smaller (more bent) than that of the trans form (MP2 178.7 °, B3LYP 178.5 °).

For the cis isomer the calculated S$_0$−S$_1$ excitation energies are 35693 cm^{-1} on the CASSCF(10,9) level, including Zero point correction. For trans o-cyanophenol this value amounts to 35737 cm^{-1}. With additional CASPT2 calculations on the CASSCF optimized structures these values amount to 32310 and 32675 cm^{-1}, respectively. Our results are comparable to

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TABLE 1: Calculated (CASSCF) Structures of *cis*- and *trans*-*o*-Cyanophenol in the S_0 and S_1 State[a]

	cis-*o*-cyanophenol			trans-*o*-cyanophenol		
	S_0	S_1	difference	S_0	S_1	difference
			bond			
$C-C_{mean}$	139.9	143.3	3.5	139.8	143.3	3.5
$C-H_{mean}$	108.1	107.9	−0.2	108.1	107.9	−0.2
C−O	134.5	133.6	−0.9	134.6	133.7	−0.9
O−H	94.7	94.9	0.1	94.5	94.6	0.1
C−CN	144.4	141.8	−2.6	144.2	142.0	−2.2
C−N	114.9	115.4	0.6	114.8	115.1	0.5
			angle			
C−C−N	177.4	177.1	−0.3	178.2	178.2	0.0
C−O−H	111.7	111.8	0.1	110.8	111.0	0.2

[a] Bond lengths are given in picometers, angles in degrees. The CCN angles in the S_0 state on the MP2 level are 175.9° (cis) and 178.7° (trans).

the vertical transition energies of 38916 cm^{-1} (CASSCF) and 35270 cm^{-1} (CASPT2) calculated for cis-*o*-cyanophenol by Granucci et al.[12] Calculations of the trans form were not reported there.

3.2. Molecular Structure. According to the CASSCF calculations, the absolute geometry of both isotopomers differs only in the orientation of the hydroxyl group. Bond lengths are almost identical, cf. Table 1. Upon excitation from the S_0 to the S_1 state the mean C−C distance increases by 3.5 pm whereas the C−H distances decrease by averaged 0.2 pm. The C−O bond becomes 0.8 pm and the C−N bond 0.6 pm shorter (0.5 pm for the trans isomer). The strongest change in geometry is found as a shortening of the C−CN bond by 2.2 pm.

3.3. Calculated Normal Modes. Table 2 shows the calculated harmonic frequencies from the MP2 and DFT calculations for the electronic ground state and the CASSCF results for the first electronically excited state of *cis*- and *trans*-*o*-cyanophenol. The CASSCF frequencies of the ground state are given for comparison. Note the small difference between most of the calculated normal-mode frequencies of the two rotational isomers.

A scheme of the normal modes discussed below is displayed in Figure 2. The nomenclature is based on Varsanyi's numbering for ortho-di-light substituted benzenes.[13] The modes 15 and 9b which are asymmetric and symmetric bending modes in symmetric ortho-di-light aromatics split into a bending mode of the COH group (δC−OH) and of the CCN group (δC−CN), respectively. To avoid confusion with the δCC−N bending modes, we use the labels 15 and 9b. Modes 7a and 13 (symmetric and antisymmetric stretching modes of the substituent) become the stretching mode νC−CN and νC−OH, respectively. Additionally, the C−CN stretching vibration shows also contributions from a CO−H bending. (The complete results of our calculations can be accessed via our homepage http://www.-public.rz.uni-duesseldorf.de/~pc1/abinitio.)

4. Experimental Results

Figure 3 shows the laser-induced fluorescence (LIF) spectrum of *o*-cyanophenol from 33900 to 35300 cm^{-1}. The stars mark the transitions analyzed by dispersed fluorescence (DF) spectroscopy. We found the electronic origin at 33954 cm^{-1}. This

TABLE 2: Calculated Frequencies (in cm^{-1}) of *cis*- and *trans*-*o*-Cyanophenol

	S_0						S_1	
mode	B3LYP 6-311G(d,p)		MP2 6-311G(d,p)		CAS(10,9) cc-pVDZ		CAS(10,9) cc-pVDZ	
10b	132	128	127	121	136	131	107	103
δCC−N	141	154	133	146	159	168	157	165
10a	236	237	220	221	245	246	195	194
τOH	435	359	342	263	353	288	382	334
16b	403	591	379	577	389	383	287	431
15	390	375	384	369	415	400	399	386
γCCN	588	402	485	374	498	495	440	286
9b	474	471	466	461	511	503	491	479
16a	511	509	423	411	569	574	409	402
6a	569	567	561	559	601	600	563	562
6b	614	611	602	599	661	658	647	643
4	749	752	570	479	750	752	526	530
1	740	740	737	737	771	772	737	737
11	771	764	750	740	781	777	591	568
17b	965	957	834	812	882	870	621	607
12	859	857	851	850	923	924	897	896
17a	877	856	893	883	970	965	672	645
5	995	989	900	894	1007	1001	752	745
18b	1052	1062	1054	1062	1095	1102	1036	1040
18a	1117	1115	1113	1112	1173	1176	1120	1128
9a	1179	1186	1179	1183	1263	1267	1241	1245
δ O−H	1247	1192	1200	1196	1283	1279	1259	1253
νC−CN	1199	1232	1257	1241	1358	1339	1346	1330
νC−OH	1280	1293	1293	1312	1385	1392	1372	1367
3	1338	1329	1357	1334	1450	1442	1431	1424
14	1373	1359	1452	1450	1577	1569	1540	1535
19b	1498	1485	1501	1487	1656	1664	1601	1604
19a	1516	1535	1526	1540	1738	1733	1713	1729
8a	1615	1628	1632	1644	1816	1823	1766	1762
8b	1657	1648	1669	1658	1853	1847	1827	1831
νC−N	2321	2340	2186	2191	2544	2559	2506	2530
νC−H	3177	3158	3215	3197	3329	3307	3350	3335
νC−H	3190	3181	3225	3219	3336	3330	3362	3352
νC−H	3201	3192	3237	3227	3338	3339	3367	3363
2	3206	3205	3243	3242	3366	3357	3381	3378
νO−H	3765	3831	3823	3876	4124	4161	4104	4143

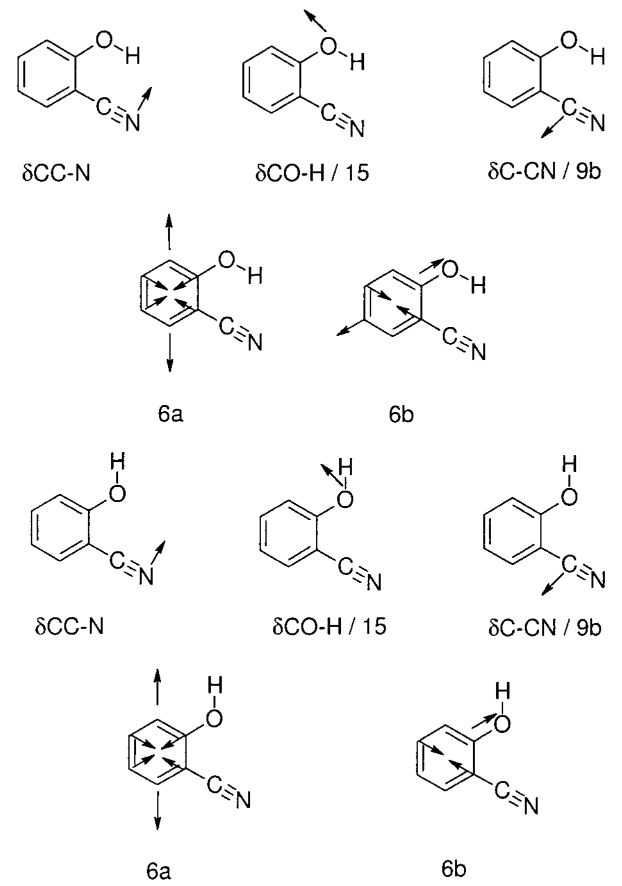

Figure 2. Displacement scheme of some normal modes of *o*-cyanphenol.

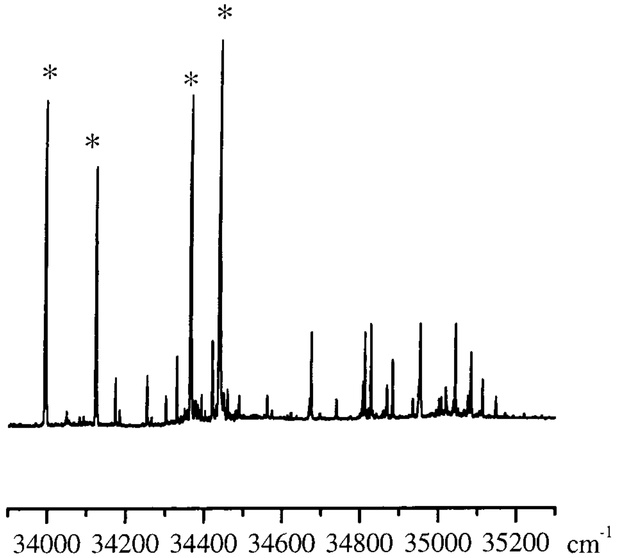

Figure 3. Fluorescence excitation spectrum of *o*-cyanophenol. The stars mark the excitation positions for obtaining the dispersed fluorescence spectra.

is the redmost band in the spectrum and agrees with the value cited in ref 12.

4.1. Dispersed Fluorescence Spectra. The dispersed fluorescence spectra of the bands at 0, +128, +371, and +445 cm^{-1}relative to the origin of *o*-cyanophenol are shown in Figure 4.

The most intense band in the DF spectrum of the electronic origin at 464 cm^{-1} is assigned to the C−CN bending mode 9b. The δCC−N vibration and its first overtone can be seen as the first two bands of this spectrum at 134 and 269 cm^{-1}, respectively. Other intense bands are assigned to the ring deformation mode 6b at 598 cm^{-1}, the stretching modes νC−CN (1262 cm^{-1}), and νC−OH (1312 cm^{-1}), and their combinations with bending modes. The DF spectrum taken at 128 cm^{-1} above the electronic origin shows a very intense band at 134 cm^{-1}, the δCC−N mode. The first overtone at 269 cm^{-1} is still very intense and the second overtone (404 cm^{-1}) can also be found. The band at 128 cm^{-1} can be assigned to the δCC−N mode in the S$_1$ state according to the propensity rule. Beside several combination bands with the δCC−N mode, we observe the fundamentals of the vibrations 9b, 6b, 1 (735 cm^{-1}), and combination bands thereof.

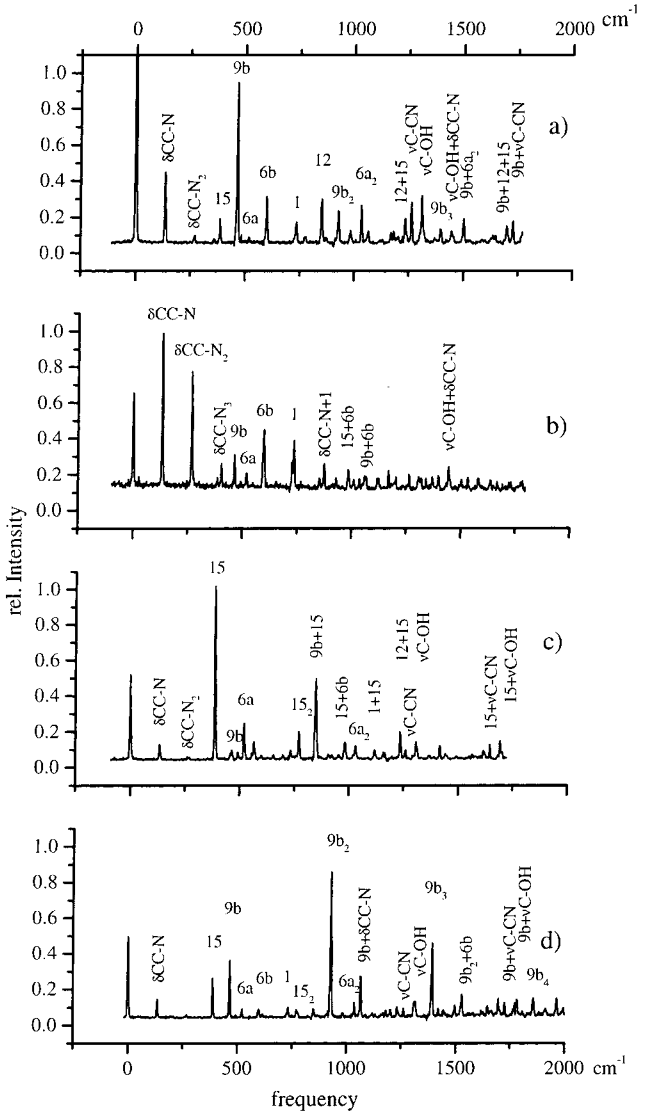

Figure 4. Dispersed fluorescence spectra of the (a) 0_0^0, (b) the band at + 128 cm^{-1}, (c) 371 cm^{-1}, and (d) 445 cm^{-1} of *o*-cyanophenol. For the most important bands the assignment is given.

Spectrum c taken at 371 cm^{-1} above the electronic origin is dominated by mode 15 (δC−OH). Its fundamental at 386 cm^{-1} is the most intense band and almost all the other transitions of some intensity are combination bands with mode 15. The weaker bands stem from the δCC−N bending mode, the stretching modes and mode 6a.

The progression of vibration 9b is most important in the DF spectrum obtained from excitation at 0_0^0 + 445 cm^{-1}. The first overtone is about twice as intense as the fundamental and the

TABLE 3: Assignment of the Observed Frequencies (in cm^{-1}) in the Dispersed Fluorescence Spectra

134	δCC−N	1262	νC−CN
269	δCC−N$_2$	1304	3
359		1312	νC−O
386	15	1369	$15_2 + 6b$
404	δCC−N$_3$	1371	$12 + 15 + \delta$CC−N/9b + $15_2 + \delta$CC−N
456	x[a]	1387	
464	9b	1395	$9b_3$/νC−CN + δCC−N
519	15 + δCC−N	1419	$15_3 + \delta$CC−N$_2$
564	6a	1444	νC−O + δCC−N
599	6b/9b + δCC−N	1449	15 + 6b + 9b/$9b_2$ + 15 + δCC−N/ /νC−O + δCC−N
654			
700		1500	9b + $15_2 + \delta$CC−N$_2$
734	1	1531	$9b_2$ + 6b
772		1582	νC−O + δCC−N$_2$
776	15_2	1619	15_2 + 12
851	12/9b + 15	1636	9b + $15_2 + \delta$CC−N$_3$
873	1 + δCC−N	1646	νC−CN + 15
909	$15_2 + \delta$CC−N	1665	$6b_2$ + 9b
921	x + 9b	1698	12 + 15 + 9b/$9b_2$ + 15_2
929	$9b_2$	1727	9b + νC−CN
984	15 + 6b/9b + 15 + δCC−N	1766	9b + 3
1010		1772	9b + νC−O
1034	$15_2 + \delta$CC−N$_2$	1781	
1064	9b + 6b/$9b_2$ + δCC−N	1843	
1120	15 + 1	1856	$9b_4$
1170	$15_2 + \delta$CC−N $_3$	1911	15 + 6b + $9b_2$/$9b_3$ + 15 + δCC−N/ /9b + νC−O + δCC−N
1203	$6b_2$	1964	$9b_2 + 15_2 + \delta$CC−N$_2$
1234	12 + 15/9b + 15_2	1991	$9b_3$ + 6b

[a] This band cannot be assigned. The label "x" stands for assignment of combination bands.

second overtone. The other bands are assigned as before. We also observe some combination bands with mode 9b.

The assignment of all observed transitions is summarized in Table 3.

5. Conclusions

On the basis of our results from the dispersed fluorescence spectra, we assign the bands at 128, 371, and 445 cm $^{-1}$ in Figure 3 to the transitions δCC−N$^1_0$, 15^1_0, and $9b^1_0$ respectively. Note that the fluorescence into the corresponding fundamental or overtone vibrational state is much more intense than the resonant transition. (We have to mention that even with background correction there is still scattered light. This pretends an even greater intensity in the resonance peak.) In the case of the 9b spectrum the first overtone is even the most intense band. The difference between the calculated normal modes of the two isomers is too small to determine the corresponding isomer from it. However, the calculated frequencies for mode δCC−N and mode 15 of the cis form match the experimental values better than those of the trans form.

The DF spectra are dominated by bands belonging to bending modes and to their combination bands and overtones. Therefore, it is fair to assume that the geometry of *o*-cyanophenol changes toward a bent structure upon excitation from the S_0 to the S_1 state. The calculations, however, do not predict such a geometry change, for neither of the two rotamers. They do show a decrease of electron density between the N atom and the C atom of the cyano group and an increase of electron density between the CN group and the aromatic ring. In other words, the C−N bond has less triple bond character in the S_1state whereas the C−CN bond shows more double bond character. This may also change the CCN angle somewhat explaining the strong Franck−Condon activity of the CCN bending modes.

6. Summary

Dispersed fluorescence spectra have been recorded from excitation of four S_1state levels of *o*-cyanophenol. The assignment of the ground state is based upon ab initio calculations on the MP2 and DFT level (6-311G(d,p) basis set). On the basis of the DF spectra several transitions could be assigned. From the band intensities in the DF spectra it can be deduced that the examined transitions stem from the cis form of *o*-cyanophenol. This is in agreement with the ab initio calculations which predict the cis isomer to be more stable. According to the calculated excitation energies, the spectrum of the trans form lies within the examined spectral region. It is likely that its vibronic spectrum consists of the less intense bands in our LIF spectrum. Further measurements using spectral hole burning wil clearify this point.

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