n n

LIF excitation spectra of jet-cooled 3,5-dicyanoaniline[†]

Przemysław Kolek,^a Katarzyna Pirowska,^a Łukasz Chacaga^b and Jan Najbar^{*a}

^a Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry,

- Jagiellonian University, 3 Ingardena, 30-060 Cracow, Poland
- ^b Department of Organic Chemistry, Faculty of Chemistry, Jagiellonian University,

3 Ingardena, 30-060 Cracow, Poland. E-mail: ucnajbar@kinga.cyf.kr.edu.pl

Received 23rd May 2003, Accepted 12th August 2003 First published as an Advance Article on the web 27th August 2003

The infrared and Raman spectra for crystalline 3,5-dicyanoaniline (3,5-DCA) and the laser induced fluorescence (LIF) excitation spectra of vacuum jet cooled molecules have been investigated. The ground $S_0(A_1)$ and excited $S_1(B_2)$ state geometries, charge distributions and vibrational frequencies of 3,5-DCA have been evaluated by *ab initio* calculations. The Dushinsky matrices have been used for the mode correlation and assignments of the transition frequencies in LIF excitation spectra of 3,5-DCA ($-NH_2$) and 3,5-DCA($-ND_2$) as well as the IR and Raman spectra for deuterated species. It has been found that the transitions I_0^2 involving inversion motion of the amino group in 3,5-DCA show remarkable intensities suggesting substantial change in the potential energy function upon electronic excitation for the out-of-plane motion of the hydrogen atoms in the amino group. The barrier height for the inversion in the ground electronic state of 3,5-DCA seems to be the same order as the zero point energy. For the lowest excited electronic state the potential function for the inversion has single minimum but shows substantial anharmonicity. The intensity distribution in the LIF excitation spectrum has been modeled using multidimensional Franck–Condon factors. Geometry changes for $S_0 \rightarrow S_1$ excitation of 3,5-DCA are discussed.

1. Introduction

Aniline and its derivatives are of fundamental interest in spectroscopy.^{1–8} They undergo substantial geometry changes between the ground and excited electronic states. The ground state potential energy function of aniline shows a double minimum in the inversion mode.^{9,10} In the lowest singlet excited state the corresponding potential function in the inversion mode has very small barrier at planar geometry. The laser induced fluorescence (LIF) excitation spectra of jet-cooled aniline molecule show significant intensity of the bands related to the inversion mode.^{8–10}

The changes of hybridization of the nitrogen atom in the amino group occurring due to substitution of a molecular group or electronic excitation of aniline derivatives are important topics in the fields of photochemistry and photobiology. Particularly, large geometrical transformations of the excited 4-cyano-*N*-dimethylaniline molecule and its derivatives have attracted much attention.^{12,14–16} The most important effect involves rotation of the dimethylaniline. Recently, photophysics and spectroscopy of the vacuum-isolated jet-cooled 4-cyano-*N*-dimethylaniline and related molecules have been reviewed by Phillips.¹²

Possible effects due to changes in the hybridization on the carbon atom of cyano group were suggested by Sobolewski and Domcke.¹⁷ Although this latter change of hybridization is not responsible for the appearance of dual fluorescence of 4-cyano-*N*-dimethylanilines, as originally suggested by Sobolewski and Domcke, it may, however, contribute to the presence of progressions in bending mode of CCN group in

aniline derivatives. LIF excitation spectra and dispersed fluorescence of 3-cyano- and 4-cyanoanilines were investigated by Phillips and coworkers.^{18–20} LIF excitation spectra of jetcooled 2-cyanoaniline and 3-cyanoaniline were recently studied by Kolek *et al.*²¹ The presence of the CCN bending mode has been identified in the LIF excitation spectra of 3-cyanoaniline and 2-cyanoaniline. Roth *et al.*²² in their study of 4-cyanophenol have found substantial change in geometry of the cyano group upon excitation. The strongest effect has been found in the LIF excitation spectra of *ortho*-substituted aniline derivatives: 2-cyanoaniline.²¹ 2,6-dicyanoaniline ²³ and 2,6dicyano-3,5-dimethylaniline.²⁴ Their LIF excitation spectra are dominated by long progressions in the C-CN bending mode forming combinations with other fundamental modes. Moreover, in the LIF excitation spectrum of 2,6-dicyanoaniline totally symmetric stretching fundamental mode of cyano groups have been identified.²³

The purpose of this paper is to investigate the potential energy functions in the S_0 and S_1 states of 3,5-dicyanoaniline using *ab initio* quantum mechanical calculations and IR, Raman and LIF spectroscopic techniques. Due to molecular structure of 3,5-dicyanoaniline intramolecular hydrogen bonding in the jet-cooled molecule is impossible. Thus, comparisons of the spectroscopic properties of 2,6-dicyanoaniline and 3,5dicyanoaniline make it possible to reveal these features which are influenced by intramolecular hydrogen bonding.

The potential energy function for the inversion of the amino group in aniline and its derivatives substituted in the benzene ring is symmetrical with respect to reflections in the molecular plane. The lowest state vibrational wave function for the inversion mode is also symmetrical with respect to this reflection. For the vacuum-isolated jet-cooled aniline in its lowest vibrational level the molecular geometry is bipyramidal, with C_{2v} symmetry. From the spectroscopic evidence the tunneling splitting for aniline is 40 cm⁻¹ and 12 cm⁻¹ for deuterated

[†] Electronic supplementary information (ESI) available: Analysis of the LIF spectra of 3,5-DCA(–NH₂) and 3,5-DCA(–ND₂). See http://www.rsc.org/suppdata/cp/b3/b305797f/

aniline $(-ND_2)$.^{9,11} From the quantum mechanical *ab initio* studies we find that for aniline derivatives containing substituent in the benzene ring the barrier for inversion is usually lower,²¹ thus, the resultant tunneling splitting is larger and the tunneling rate should also increase. On the other hand, substitutions of the hydrogen atoms in the amino group by heavier molecular groups reduce the tunneling rates and average hybridization of the nitrogen atom becomes pyramidal. Similar effects may result from the hydrogen bonding and perturbing by external fields in crystalline phases.

In this paper we present: (i) the results of experimental studies of the LIF excitation spectra for 3,5-dicyanoaniline and its deuterated $(-ND_2)$ derivative in the supersonic molecular beams and the corresponding ground state IR and Raman spectra, (ii) *ab initio* calculations of the molecular geometry and harmonic vibrational frequencies for these geometries which correspond to the stationary points of the potential energy functions for the ground electronic state and the lowest electronic excited state, (iii) correlations of the vibrational frequencies in the ground state and S₁ excited state of 3,5-DCA, and (iv) modeling of the intensity distributions in the LIF excitation spectra of 3,5-DCA($-NH_2$), 3,5-DCA($-ND_2$) taking into account the displacements of normal coordinates, frequency changes and mode mixing.

2. Experimental

For the excitation of the fluorescence emission, a HY 400 Nd:YAG laser and a dye laser DY 300 (Lumonics) were used. The 3,5-DCA($-NH_2$) and 3,5-DCA($-ND_2$) fluorescence was excited by the frequency doubled (BBO) output of the dye laser operating on DCM and rhodamine 640 supplied by Exciton. The pulses at 10 Hz were 10 ns in duration and had 20 μ J (or less) of energy per pulse, with a band width of about 0.1 cm⁻¹. The laser beam was introduced into a vacuum chamber and crossed the seeded supersonic expansion 10 mm downstream from an orifice having 0.5 mm internal diameter. Jet expansion was controlled by a General Valve device. A CAMAC 712 pulse analyzer was used to measure pulses delivered from a Thorn EMI 9558QB photomultiplier cooled at 245 K. Helium carrier gas was dried using a trap with liquid nitrogen. The sample injection system was heated at 120 °C.

Synthesis of 3,5-cyanoaniline was accomplished by the following procedure. A mixture of 3,5-dibromoaniline (6.3 g, 25.1 mmol), copper(1) cyanide (8.6 g, 95.6 mmol) and dimethylformamide (15,0 mL) was refluxed with vigorous stirring for 4 h. The mixture was cooled and a solution of sodium cyanide (17.2 g, 350.9 mmol) in water (60.0 mL) was added. A precipitated solid was filtered off and washed with water. The filtrate was extracted with ethyl acetate (4×30.0 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. Combined portions of crude 3,5-dicyjanoaniline were purified by vacuum sublimation and then by crystallization from petroleum ether, yield 0.9 g (25%); mp 192–194 °C. These values compare favourably with available data^{25,26} mp. 189–190 °C.

Spectroscopic data: ¹H NMR (500 MHz, DMSO- d_6) 6.12 (s, 2H), 7.15 (d, 2H, J = 1.4 Hz), 7.39 (t, 1H, J = 1.4 Hz); ¹³C NMR (125 MHz, DMSO- d_6) 113.08, 117.72, 120.08, 121.15, 150.13; IR max/cm⁻¹: 435, 672 865, 1328, 1343, 1443 1599, 1630, 2230, 3344, 3463, detailed discussion in the Results and discussion section.

Deuterium exchange in the 3,5-DCA was achieved by boiling with deuterated ethanol (C_2H_5OD) with a small amount of D₂O. FTIR spectra of the 3,5-DCA powdered samples, pressed in KBr pellets, were measured with a Brucker IFS 48 instrument. Raman spectra of the solid samples were measured using a Digilab 2000 instrument with 1064 nm excitation and FT detection. Quantum mechanical calculations using the GAUSSIAN98 program package^{27,28} were performed at the Academic Computer Center on a SGI ORIGIN2800 computer. The *ab initio* HF and CIS methods with $6-31++G^{**}$ basis functions were used for calculations of molecular structure and vibrational frequencies at equilibrium geometries. Vibrational frequencies were calculated for 3,5-cyanoaniline and its deuterated ($-ND_2$) forms in the ground and S₁ excited states. Calculated normal mode coordinates were used to derive the rotation matrices of the normal mode coordinates for each compound. The rotation matrices) were calculated for electronic transitions and for each pair of deuterium exchanged species.

Calculations of the multimode Franck–Condon factors and relative transition probabilities for the LIF excitation spectra have been performed using the recurrence equations derived by Ruhoff.^{31,32} For this purpose appropriate programs in the MATLAB calculation environment have been developed. The vibrational band intensities were calculated in two ways: (i) using all input data from the *ab initio* quantum mechanical calculation, and (ii) the displacement parameters for the totally symmetric modes have been optimized to get the best agreement with the experiment using all other parameters from the *ab initio* calculation. Minimization procedures for the sum of the least squares were used for evaluation of the displacement parameters of the normal vibrational modes for the 3,5-DCA(–NH₂) and 3,5-DCA(–ND₂) molecular species.

3. Results and discussion

3.1. Molecular geometry

According to Gordon et al.,9 in the aniline molecule in its ground state the barrier height for inversion is 526 cm⁻¹ and the tunneling splitting amounts 41 cm⁻¹. The *ab initio* molecular geometries for the ground electronic state (HF/ 6-31++G**) and the lowest S_1 electronic state (CIS/6- $31++G^{**}$) for 3,5-DCA, 2,6-DCA and aniline have been compared in Table 1. The HF/6-31++G** calculation predicts pyramidal geometry of the amino group in the ground state of 3,5-DCA. This result resembles the situation for the aniline molecule. Due to high tunneling rate for inversion in vacuum isolated aniline derivatives an average molecular geometry is bipyramidal with C_{2V} symmetry. The relevant tunneling rates are higher than 1 ps⁻¹. The electronic $S_0 \rightarrow S_1$ transition rates for the molecules considered here are order of 0.1 ns^{-1} . To take into account this effect, resulting from the nuclear motions, we have also performed the HF calculations of the nuclear geometries imposing planarity on the aniline, 3,5-DCA and 2,6-DCA molecules in their ground electronic state. For these reasons in Table 1 the results of the $HF/6-31++G^{**}$ calculated bond lengths and angles for the stationary saddle point corresponding to the planar geometry of 3,5-DCA have been included. The results concerning the ground state vibrations of the 3,5-DCA molecule calculated for these two stationary points, corresponding to the pyramidal and planar (bipyramidal) geometries, have been compared in Tables 2 and 3 for the native and deuterated forms.

From Tables 2 and 3 we find that the frequencies of vibrational modes calculated for the pyramidal and planar 3,5-DCA molecules are very similar when the same isotopic species are compared. Large discrepancies occur for the inversion mode. This is because the inversion motion in the double minimum potential is highly anharmonic. The calculated frequencies for the inversion mode merely reflect the details of the potential function for inversion at the potential well and at the barrier top (imaginary frequencies). Using the HF/6-31++G^{**} method the barrier height for the inversion motion for 3,5-DCA was evaluated as 230 cm⁻¹. The barrier for the

Table 1 Ab initio geometries for 2,6-dicyanoaniline and 3,5-dicyanoaniline in the S_0 (HF/6-31++G^{**}) and S_1 (CIS/6-31++G^{**}) states. The results for planar (pl) and pyramidal (py) molecular geometries of 3,5-dicyanoaniline are given

	3,5-DCA			2,6-DCA ²³		Aniline	
	S ₀ (py)	S ₀ (pl)	S ₁ (pl)	S ₀ (pl)	S ₁ (pl)	S ₀ (py)	$S_1(pl)$
$C_1 - C_2/Å$	1.393	1.396	1.423	1.409	1.438	1.394	1.435
$C_2 - C_3 / Å$	1.387	1.378	1.408	1.389	1.409	1.385	1.364
$C_3 - C_4 / Å$	1.388	1.388	1.409	1.383	1.402	1.387	1.403
C ₂₍₃₎ –H/Å	1.075	1.074	1.073	1.075	1.072	1.077	1.071
C ₄ –H/Å	1.073	1.072	1.074	1.073	1.074	1.075	1.074
$C_1 - NH_2/Å$	1.385	1.368	1.332	1.350	1.316	1.395	1.312
N–H/Å	0.996	0.991	0.994	0.993	0.997	0.996	1.004
1	0.250	0	0	0	0	0.278	0
C–CN/Å	1.448	1.448	1.4286	1.439	1.418		
C≡N/Å	1.136	1.136	1.1412	1.138	1.144		
$C_{6} - C_{1} - C_{2} / ^{\circ}$	118.5	118.3	122.1	116.8	120.3	118.8	119.3
$C_1 - C_2 - C_3 / ^{\circ}$	120.4	120.3	118.3	121.1	119.1	120.4	119.6
$C_{2}-C_{3}-C_{4}/^{\circ}$	121.5	121.7	120.0	121.2	119.4	120.9	120.4
$C_{3}-C_{4}-C_{5}/^{\circ}$	117.8	117.6	121.3	118.5	122.6	118.7	120.8
$\theta/^{\circ}$	37.4	0	0	0	0	41.3	0.0
H−N−H/°	112.5	117.8	117.7	118.0	118.4	111.6	116.5
C–N–H/°	116.2	121.1	121.1	121.0	120.8	115.0	121.7
C–C–N–H/°	23.5	0	0	0	0	25.5	0
$C_{2(1)} - C_{3(2)} - CN/^{\circ}$	119.0	118.9	120.5	118.9	117.7	_	
$C - C \equiv N / ^{\circ}$	179.7	179.8	179.2	178.1	177.0	_	
		H H $C6$ $C1$ $C2$ $C5$ $C4$ $C3$ H	н с _{х N} с	N DO	Н		

inversion on the amino group in 3,5-DCA assumes intermediate value between those for aniline and 2,6-dicyanoaniline. The corresponding barriers calculated at the $HF/6-31++G^{**}$ level for aniline and 2,6-DCA were found equal 408 cm⁻¹ and 0 cm⁻¹, respectively.

Geometry optimization for 3,5-DCA in the excited S_1 state has been performed without any constraints concerning molecular symmetry. The results presented in Table 1 show that in the S1 excited state of 3,5-DCA the amino group assumes planar geometry, *i.e.* the potential energy function for inversion has single minimum. Moreover, upon electronic excitation remarkable changes of the interatomic distances occur especially in the vicinity of the amino group. For the changes of interatomic distances assuming the nonplanar geometry of the initial 'equilibrium' ground state we find: $C_1-C_2+3.0$ pm, C₂-C₃ and C₃-C₄+2.1 pm, C₁-NH₂-5.3 pm, C-CN - 1.9 pm. Corresponding changes of the molecular geometry calculated taking as a reference the planar geometry of the molecule in the initial ground state are the following: C1- $C_2 + 2.7$ pm, $C_2-C_3 + 3.0$ pm, $C_3-C_4 + 2.1$ pm, $C_1-NH_2 - 3.6$ pm, C–CN – 1.9 pm.

3.2. Vibrational modes

There are 42 normal modes of vibration in the 3,5-DCA molecule, 29 in-plane (15 a_1 , 14 b_2 in C_{2v}) and 13 out-of-plane (8 b_1 , 5 a_2 in C_{2v}) vibrational species. The out-of-plane modes belong to the b_1 and a_2 species. Raman spectra of the crystalline samples of 3,5-DCA(-NH₂) and 3,5-DCA(-ND₂) at room temperature are shown in Fig. 1. In Table 2 the ground state vibration frequencies for 3,5-DCA are compared with the calculated *ab initio* HF/6-31++G^{**} frequencies. The calculated vibrational frequencies in Table 2 are numbered according to increasing frequencies for each molecular species, each electronic state and each stationary point (except for the case of imaginary frequencies of the inversion motion at planar molecular geometry).

Table 2 gives also measured IR and Raman band frequencies and the calculated harmonic frequencies for the 3,5-DCA(-NH₂) whereas Table 3 contains experimental IR and Raman band frequencies for the 3,5-DCA ($-ND_2$) form. Correlations between the vibrational frequencies of the 3,5-DCA $(-NH_2)$ and 3,5-DCA $(-ND_2)$ species in their equilibrium and planar geometries have been performed using the rotation matrices of the normal coordinates for corresponding forms of 3,5-DCA in the S_0 electronic state. For the *ab initio* HF frequencies calculated using the 6-31++G** basis set the scaling factors were found to be slightly different for the in-plane vibrational modes ($f = 0.915 - 7.5 \times 10^{-6} \nu_{calc}$) and the out-of-plane vibrations.^{21,29} For the latter, a constant factor of 0.89 has been used. The same scaling factors have been applied to the vibrational frequencies in the S_1 electronic state, calculated using the $CIS/6-31++G^{**}$ method. For planar geometry of the 3,5-DCA molecule a single imaginary frequency corresponding to the inversion mode has been calculated (i 380.6 cm⁻¹ for $-NH_2$ form and i 293.0 cm⁻¹ for $-ND_2$ form).

Since IR and Raman experimental spectroscopic data refer to crystalline samples whereas calculations of the vibrational frequencies have been performed for the isolated molecule, the quality of correlation is obviously affected by contributions from the hydrogen bonding and matrix effects as well. Thus, we were unable to assign transition involving the inversion modes in our IR spectra. The frequencies for stretching

Table 2 Assignment and correlations of the molecular vibrations in the S₀ state for 3,5-DCA($-NH_2$). The calculated *ab initio* HF/6-31++G^{**} vibrational frequencies (in cm⁻¹) were scaled as described in the text. The calculated vibrational frequencies are numbered according to increasing frequencies. I_{IR} and A_{Ram} represent calculated IR and Raman intensities. Normal modes are identified by their reference to the Varsanyi description for substituted benzene derivatives²⁹

	HF/6	5-31++G*	*			Experimental							
	3,5-D	CA(-NH ₂)		3,5-D	CA(-NH ₂):	planar			IR		Ramai	1
	No	$\bar{\nu}_{\mathrm{scaled}}$	$I_{\rm IR}$	$I_{\rm Ram}^{a}$	No	$\bar{\nu}_{\mathrm{scaled}}$	$I_{\rm IR}$	$I_{\rm Ram}^{a}$	Assign	$\bar{\nu}$	$I/I_{\nu \rm CN}$	$\bar{\nu}$	$I/I_{\nu \rm CN}$
a ₁	2	118.2	10.0	229.1	2	118.4	10.0	229.1	9a C-(CN) bend.				
(a')	9	445.0	11.9	82.0	9	445.4	11.9	82.0	6a	459	< 0.1	458	0.15
	13	533.0	16.7	93.0	13	530.4	16.7	93.0	CN bend			547	0.40
	14	550.3	126.7	235.5	14	540.1	126.7	235.5	I(-NH ₂), ring def.				
	23	967.3	2.0	474.5	23	965.6	2.0	474.5	1	975	< 0.1	976	0.34
	24	988.1	17.7	245.6	24	991.2	17.7	244.4	12	1010	0.1	1008	0.06
	27	1160.3	23.8	136.3	27	1161.2	23.8	136.3	18a	1158	0.1		
	30	1315.4	58.6	745.4	30	1325.4	58.6	744.3	13	1343	0.6	1343	0.23
	31	1442.8	42.9	2.9	31	1444.9	42.9	2.9	19a	1443	0.6	1445	0.03
	33	1606.5	96.2	260.8	33	1602.8	96.2	260.8	8a	1599	1.4	1599	0.07
	35	1638.4	186.6	147.9	35	1626.7	186.6	147.9	NH ₂ scissoring	1630	2.7	1625	0.04
	37	2327.6	15.5	3035.0	37	2327.2	15.5	3035.0	νCN	2230	1.0	2232	1.00
	39	2997.6	3.8	387.6	39	2997.1	3.8	387.6	νCH	3078	0.3	3074	0.13
	40	3024.1	1.0	200.7	40	3025.2	1.0	200.7	νCH	3090	0.3	3090	0.07
	41	3380.0	49.7	483.2	41	3427.1	49.7	483.2	$\nu \mathrm{NH}_2$	3344	1.4		
b ₁	1	110.5	5.4	0.0	1	110.7	4.6	0.0	11				
(a')	5	215.1	6.1	21.1	5	213.3	3.3	18.3	10b			227	0.02
	10	436.1	21.8	61.7	10	437.8	14.5	24.3	16b	435	0.4	436	0.03
	12	507.0	165.0	42.7	12	i 369.0	277.2	1.9	ring def., I(-NH ₂)	521	< 0.1	523	0.06
	16	614.8	30.0	61.7	16	609.7	0.0	50.8	ring, CN bend.	604	0.1	616	0.05
	18	666.5	23.9	5.8	18	667.0	24.8	5.8	4	672	0.6		
	19	879.4	61.8	0.0	19	872.4	55.1	0.0	5	865	0.9		
	21	896.3	6.5	0.0	21	887.1	10.9	1.3	17b	839	0.1		
a_2	3	160.8	0.6	3.2	3	161.4	0.0	0.0	10a				
(a″)	6	243.1	17.1	7.3	6	306.5	0.0	2.1	$T(-NH_2)$				
	8	377.5	0.2	100.4	9	378.3	0.0	102.2	16a			374	0.12
	17	624.4	0.1	104.6	17	625.2	0.0	100.1	CN bend				
	22	902.0	0.0	1.3	22	893.5	0.0	1.3	17a			926	0.03
b ₂	4	170.2	0.8	111.7	4	170.5	0.4	123.2	9b C-(CN) bend				
(a″)	7	361.8	4.7	0.0	7	361.1	7.1	0.0	C-(NH ₂) bend				
	11	447.2	0.0	33.1	11	446.6	0.0	29.9	6b				
	15	628.0	0.7	23.8	16	627.5	0.5	24.1	CN bend				
	20	904.5	4.8	30.3	20	902.5	2.7	31.9	7b	855	0.2		
	25	1062.1	26.3	36.1	25	1032.5	25.8	22.7	NH ₂ bend, 14	1103	< 0.1		
	26	1142.7	4.8	4.5	26	1141.2	0.0	5.7	18b				
	28	1175.2	41.3	3.3	27	1158.7	69.1	7.8	14, NH ₂ bend	1176	0.1	1178	0.08
	29	1303.2	2.1	2.1	29	1302.9	3.2	2.1	3	1328	0.7	1333	0.05
	32	1470.5	6.2	5.7	32	1466.0	2.3	6.7	19b	1464	< 0.1	1464	0.01
	34	1617.5	15.7	387.7	34	1612.4	22.2	341.2	8b			1587	0.07
	36	2327.0	60.8	973.6	36	2326.6	61.2	955.8	νCN	2242	0.2	2242	0.34
	38	2997.4	0.7	207.3	38	2996.8	0.9	214.9	ν CH, 20b	3045	0.3	3040	0.07
	42	3475.1	33.1	138.7	42	3541.1	55.9	119.4	νNH_2	3463	1.2		

 $^{a}I_{\text{Ram}} = K(\nu)A_{\text{Ram}}$ (from calculations); $K(\nu) = 2.397497 \times 10^{-15} (\nu_0 - \nu_{\text{scaled}})^4 / (1 - \exp(-\nu_{\text{scaled}}/207.23)); \nu_0 = 9398.5 \text{ cm}^{-1}$ (incident radiation energy).

N-H modes derived from the IR spectra have slightly lower frequencies than the calculated ones. These last differences may result from hydrogen bonding in crystalline sample.

3.3. LIF excitation spectra

Vapor phase absorption spectrum of 3,5-DCA at 120 °C shows absorption bands of comparable intensities centered at 31 000 and 41 000 cm⁻¹ and strong absorption band centered at 45 500 cm⁻¹. This observation is qualitatively reproduced by the TD DFT B3LYP/6-31++G** calculation. In this evaluation three lowest excited states are as follows: S₁, 31 551 cm⁻¹ (f = 0.062), S₂, 39 455 cm⁻¹ (f = 0.033) and S₃, 41 616 cm⁻¹ (f = 0.003). These results suggest rather large separation of the S₁ (B₂) excited electronic state and the higher excited states.

Moreover, those nearest to the first excited electronic state have low transition probabilities. The results of CIS/6- $31++G^{**}$ calculation lead to similar conclusion, the excited states with large oscillator strength should occur at energies higher than 45 000 cm⁻¹.

The LIF excitation spectra of 3,5-DCA($-NH_2$) and its deuterated ($-ND_2$) form are given in Figs. 2a, and 2b, respectively, together with probable assignments of the fundamental transitions. The electronic origin for the $S_0(A_1) \rightarrow S_1(B_2)$ electronic transition in the 3,5-DCA molecule is at 30295.1 cm⁻¹. Due to deuterium exchange the electronic origin shifts to lower frequencies by -9.4 and -16 cm⁻¹ for -NHD and $-ND_2$ forms, respectively. These shifts are similar to those found for 2,6-dicyanoaniline²³ and 2,6-dicyano-3,5-dimethylaniline,²⁴ -9 and -18 cm⁻¹ for -NDH and $-ND_2$ forms, respectively

Phys. Chem. Chem. Phys., 2003, 5, 4096–4107 4099

Table 3 Assignment and correlations of the molecular vibrations in the S₀ state for 3,5-DCA(-ND₂)

	HF/6-31	$++G^{**}$					Experimental						
	3,5-DCA(-ND ₂)			3,5-E	DCA(-ND ₂)	planar			ID	Daman	ID	Domon	
_	No ^a	$\bar{\nu}_{\mathrm{scaled}}$	$I_{\rm IR}$	I_{Ram}^{b}	No	$\bar{\nu}_{\mathrm{scaled}}$	$I_{\rm IR}$	$I_{Ram}^{\ \ b}$	Assign	$\bar{\nu}$	$I/I_{\nu CN}$	$\bar{\nu}$	$I/I_{\nu CN}$
a ₁	2 (2)	118.0	10.0	229.4	2	118.2	10.1	225.0	9a C-(CN) bend				
(a′)	11 (9)	445.7	1.4	116.8	11	445.4	0.6	120.3	6a	458	0.2	461	0.17
	14 (13)	532.8	0.6	142.7	14	533.0	0.9	160.4	CN bend	538	< 0.1	539	0.26
	13 (12)	506.2	3.1	110.0	13	520.4	2.3	110.2	ring def., I(-ND ₂)	522	< 0.1	522	0.12
	24 (23)	954.1	9.6	177.3	24	954.7	2.4	313.9	1	967	0.1	968	0.30
	25 (24)	981.2	14.1	540.3	25	980.9	24.2	445.7	12	1006	0.1	1001	0.20
	27 (27)	1135.2	8.1	15.7	26	1132.4	7.8	13.5	18a	1152	< 0.1	1148	0.02
	31 (30)	1338.4	119.6	562.5	31	1353.6	152.1	600.4	13	1370	0.6	1370	0.13
	32 (31)	1443.0	61.5	5.8	32	1446.8	93.3	11.5	19a	1447	1.3	1449	0.05
	34 (33)	1609.6	198.1	357.5	34	1606.3	268.1	410.3	8a	1604	2.9	1604	0.18
	29 (35)	1210.2	21.0	334.0	29	1205.6	28.5	356.4	ND ₂ bend.,	1203	0.2	1214	0.17
	37 (37)	2327.6	15.5	3034.4	37	2327.2	15.2	3048.9	νCN	2231	1.0	2232	? 0.88
	41 (39)	2997.6	3.8	389.6	41	2997.0	4.9	398.6	νCH	3074	0.3	3070	0.34
	42 (40)	3024.1	0.9	202.3	42	3025.2	1.1	200.2	νCH	3086	0.3	3087	0.10
	38 (41)	2466.3	47.5	458.4	38	2498.7	99.4	481.4	$\nu \mathrm{NH}_2$	2446	0.6	2448	0.20
b_1	1 (1)	109.2	5.3	0.0	1	109.6	5.5	0.0	11				
(a')	6 (5)	206.3	9.9	29.9	5	207.8	1.1	23.9	10b			211	0.04
	12 (10)	447.5	25.5	33.1	12	436.7	10.9	22.6	16b	434	0.5	435	0.04
	9 (14)	407.9	169.5	58.3	7	i 284.3	154.9	0.0	I(-ND ₂), ring def.				
	16 (16)	612.1	8.1	52.8	16	607.3	0.5	52.4	ring, CN bend.	600	0.3	615	0.08
	18 (18)	666.5	22.8	5.8	18	666.9	23.7	5.8	4	668	0.7		
	20 (19)	878.9	61.1	0.0	20	872.2	58.4	0.0	5	853	0.6		
	21 (21)	896.2	6.9	0.0	21	887.1	10.7	1.3	17b	839	0.7	839	< 0.01
a_2	3 (3)	154.4	2.3	10.0	3	159.0	0	0.0	10a				
(a″)	5 (6)	181.0	6.7	11.9	6	221.4	0	2.6	$T(-ND_2)$				
	8 (8)	376.9	0.1	96.7	9	377.0	0	96.7	16a			374	0.14
	17 (17)	623.9	0.0	106.1	17	624.3	0	103.1	CN bend.				
	22 (22)	901.8	0.1	0.0	22	893.0	0	1.3	17a			945	0.04
b ₂	4 (4)	166.0	1.1	91.7	4	165.6	0.4	119.4	9b C-(CN) bend.				
(a″)	7 (7)	335.9	3.1	2.0	8	332.2	6	0.0	$C-(ND_2)$ bend.				
	10 (11)	444.9	0.1	33.1	10	444.0	0	31.8	6b			452	0.04
	15 (15)	618.6	1.0	19.5	15	616.2	0.8	21.2	CN bend				
	23 (20)	924.3	8.3	57.5	23	920.7	7.8	51.9	7b	880	0.2	880	< 0.01
	19 (25)	847.1	0.1	1.3	19	826.3	0.2	1.3	ND_2 bend., 14				
	28 (26)	1145.2	36.1	0.0	28	1147.2	51.3	1.1	18b	1147	0.1		
	26 (28)	1134.7	32.5	20.2	27	1132.5	38.1	19.3	14, ND_2 bend.			1177	0.02
	30 (29)	1301.9	2.5	2.1	30	1301.9	3.4	2.1	3	1326	0.7	1329	0.03
	33 (32)	1452.9	4.5	2.9	33	1452.2	2	2.9	19b				
	35 (34)	1614.4	16.9	390.1	35	1610.2	22.2	345.2	8b			1583	0.08
	36 (36)	2327.0	60.7	973.6	36	2326.6	61.2	955.2	νCN	2243	0.7	2243	? 1.00
	40 (38)	2997.4	0.7	208.1	40	2996.8	0.9	215.3	νCH, 20b			3025	0.05
	39 (42)	2591.8	17.5	115.3	39	2647.7	28.8	102.1	νNH_2	2589	2.3	2597	0.06
^{<i>a</i>} In j calcul	parentheses lations); <i>K</i> (the numb (ν) = 2.397	ering of the formula	he corresp $^{-15}(\nu_0 - \nu$	onding _{scaled}) ⁴ /	normal mo $(1 - \exp(-i))$	des for 3,5 v _{scaled} /207	5-DCA(-NI 7.23)); $\bar{\nu}_0 =$	H ₂) is given (column 2 9398.5 cm ^{-1} (inciden	in Table t radiatio	2). ^b I_{Ram} = on energy).	$= K(\nu)A_{\rm c}$	_{Ram} (from

and about two times larger than the deuteration shifts for 3-cyanoaniline -5 and -7 cm⁻¹, respectively.²¹

The vibrational lines in the LIF excitation spectra of 3,5-DCA have FWHH around 1.4–1.7 cm⁻¹. In the spectral range 2250 cm⁻¹ above the electronic origin for 3,5-DCA almost 140 spectral lines have been found. Table Ia of the electronic supplementary information (ESI)[†] lists vibrational band positions in the LIF excitation spectrum of 3,5-DCA($-NH_2$), their relative integral intensities (column 6) and the assignment of the transitions based on the results of the CIS/6-31++ G^{**} calculation (columns 4 and 5). In column 2 the analysis of the LIF excitation spectrum in terms of fundamental experimental frequencies is given. In column 3 the differences between the observed frequencies and the assigned combinations of fundamental frequencies are shown. For correlation of vibrational modes in the ground S₀ and excited S₁ states, the Dushinsky matrices, R_{ii} , describing transformations of normal modes upon electronic excitation were employed. (See Appendix A and Table 4.)

Table Ib (ESI)† lists vibrational band positions in the LIF excitation spectra of 3,5-DCA($-ND_2$) and 3,5-DCA(-NHD), their relative integral intensities (column 6) and the assignment of the observed transitions based on the results of the CIS/6-31++G** calculation. Table Ib (ESI) is organized in the same way as Table Ia (ESI). The relative band intensities for 3,5-DCA(-NHD) are listed relative to the 00 transition for the 3,5-DCA($-ND_2$) species. The last two columns give the calculated transition intensities in the LIF excitation spectrum of 3,5-DCA($-ND_2$).

Correlations between the normal modes calculated for the ground S₀ electronic state and the first excited electronic state S₁ of the planar 3,5-DCA molecule (for the assumed C_{2v} symmetry in both states) are displayed in Table 4. In Table 4 the four diagonal blocks of the Dushinsky matrix are shown: $a_1 \times a_1$, $b_1 \times b_1$, $a_2 \times a_2$ and $b_2 \times b_2$. The off-diagonal blocks are not shown, because they are zero blocks. The vibrational modes are numbered according to increasing frequency in



Fig. 1 Raman spectra of 3,5-DCA(-NH₂) and 3,5-DCA(-ND₂) in crystalline phases at room temperature.

each electronic state. The correlations shown in Table 4 are based on the largest projections of normal coordinates in the corresponding electronic states. The vibrational modes are arranged in such a way that the largest overlap appears on the diagonal of the matrix. In Table 4 the displacements of the normal coordinates under $S_0 \rightarrow S_1$ excitation for the totally symmetric vibrations a_1 are included.

Table 4 gives explicit evidence of mode mixing upon electronic excitation. A mode mixing is predicted among skeleton modes, especially among modes revealing large frequency



Fig. 2 LIF excitation spectrum of jet-cooled 3,5-dicyanoaniline in native form 3,5-DCA($-NH_2$) (a) and in deuterated form 3,5-DCA($-ND_2$) (b). The bands are indicated by their frequencies in cm⁻¹ relatively to the band origin: 30295.1 cm⁻¹ for 3,5-DCA($-NH_2$) and 30279.2 cm⁻¹ for 3,5-DCA($-ND_2$).

Table 4 Normal mode displacements and diagonal blocks $a_1 \times a_1$, $b_1 \times b_1$, $a_2 \times a_2$ and $b_1 \times b_1$ of the Dushinsky matrix for the $S_0(A_1) \rightarrow S_1(B_2)$ electronic transition calculated using HF/6-31++G^{**} and CIS/6-31++G^{**} methods for the 3,5-DCA molecule. The vibrational modes and stationary point molecular geometries are calculated for planar 3,5-DCA molecules in the S_0 and S_1 electronic states

		S	a ₁														
K_i	S_1	pl No	2 2	10 9	13 13	14 14	23 23	24 24	28 27	30 30	31 31	33 33	35 35	37 37	39 39	40 40	41 41
-0.249 0.255 -0.066 0.229 0.13 0.055 -0.049 -0.124 -0.049 -0.015 0.003 0.022 -0.000 0.000	9 4 6 0 7 2 3 3 4 0 5 5 8 3 7 7 0 7	3 12 17 14 23 24 27 30 31 34 35 37 39 40 41	-100 2 -1 -1 1	$ \begin{array}{r} -2 \\ -100 \\ 3 \\ 7 \\ 1 \\ 2 \\ 1 \\ -1 \\ \end{array} $	$ \begin{array}{r} -3 \\ -100 \\ -6 \\ -2 \\ 1 \\ 1 \\ 2 \\ 1 \\ -1 \\ -2 \\ \end{array} $	$ \begin{array}{c} 1 \\ -7 \\ 7 \\ -99 \\ -3 \\ -2 \\ 1 \\ -1 \\ 1 \\ -1 \end{array} $	$ \begin{array}{r} 1 \\ -99 \\ -4 \\ -7 \\ 1 \\ -6 \\ -4 \\ 2 \end{array} $	-1 1 -1 2 -98 19 1 6 7 -4	$ \begin{array}{r} -1 \\ 1 \\ -8 \\ 19 \\ 97 \\ -6 \\ 3 \\ -3 \\ 1 \\ 2 \\ \end{array} $	$ \begin{array}{r} -1 \\ 2 \\ -1 \\ -2 \\ 4 \\ -3 \\ 7 \\ 74 \\ -66 \\ -3 \\ 10 \\ 1 \\ -1 \end{array} $	-2 5 -6 -67 -72 -15 7 2 1	$ \begin{array}{r} 1 \\ -3 \\ 4 \\ -4 \\ -8 \\ -13 \\ 98 \\ 14 \\ 1 \\ -1 \end{array} $	1 -2 3 -4 1 -14 12 -98 -1	-1 2 1 -1 -2 1 -100	2 -1 -2 -99 -16	16 _99	1
c		S ₀ pl	b ₁ 1		5		12		8		15		18		19		21
b ₁		2 5 13 7 15 8 20 22	-	98 16 -1 -2 5 1 -1	$ \begin{array}{r} -15 \\ -98 \\ 3 \\ -4 \\ -1 \\ 10 \\ -4 \\ 2 \end{array} $		$ \begin{array}{r} 6 \\ 9 \\ 52 \\ -3 \\ -45 \\ 71 \\ -2 \\ 2 \end{array} $		-20 -97 -2 -2 -2 -2 -2 -2 -2 -2		$ \begin{array}{r} 2 \\ -3 \\ -59 \\ 14 \\ -77 \\ -4 \\ 18 \\ 1 \end{array} $		$ \begin{array}{r} 4 \\ 3 \\ -54 \\ 17 \\ 44 \\ 68 \\ 13 \\ -1 \end{array} $		$ \begin{array}{r} 1 \\ 4 \\ -20 \\ 3 \\ -7 \\ 7 \\ -97 \\ 4 \end{array} $		$ \begin{array}{r} 1 \\ -2 \\ 1 \\ -3 \\ 2 \\ -4 \\ -100 \\ \end{array} $
S_1			S ₀ pl No		$\frac{a_2}{3}$			6			9 8			17 17			22 22
a ₂			1 10 6 16 18		-85 7 -52 -6			-7 83 19 21 48			50 27 -75 -32 5			13 -14 -35 92			-1 47 7 10 -87
S ₁	S ₀ pl No	b ₂ 4 4	7 7	11 11	16 15	20 20	2:	5	26 26	27 28	29 29	32 32	34 34	36 36	- 	38 38	42 42
b ₂	4 9 11 19 21 25 26 33 29 32 28 36 38 42	-100 -3 -3 -11 1 1 -1	$ \begin{array}{r} 3 \\ -100 \\ 7 \\ 4 \\ 1 \\ -2 \\ 1 \\ 4 \\ -1 \\ -1 \\ 1 \\ \end{array} $	$ \begin{array}{c} 3 \\ -7 \\ -99 \\ -1 \\ -8 \\ 3 \\ 2 \\ -3 \\ 3 \\ 1 \end{array} $	$ \begin{array}{r} -4\\2\\-99\\-2\\-9\end{array} $	8 -99 -4 (-2 -1) -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1	3	-2 7 3 83 34 24 4 10 34	$ \begin{array}{c} -1 \\ -2 \\ 0 \\ 0 \\ -5 \\ 27 \\ -87 \\ -8 \\ -18 \\ 17 \\ -30 \\ 1 \\ 1 \end{array} $	$ \begin{array}{c} 1\\3\\-4\\-5\\-13\\-27\\81\\30\\-38\\7\\-1\end{array} $	$ \begin{array}{c} 1 \\ 0 \\ -2 \\ 1 \\ 4 \\ 1 \\ 26 \\ -87 \\ -8 \\ 42 \\ -2 \end{array} $	$ \begin{array}{r} 1 \\ -4 \\ 4 \\ -1 \\ -24 \\ 3 \\ -24 \\ -25 \\ -76 \\ -49 \\ \end{array} $		1 3 3 6 6 3 8 8 8 8 8 8 8 8 8 8 8 8 9 9 9 0 0 7 7 2	$ \begin{array}{c} 1 \\ -1 \\ 3 \\ -3 \\ -2 \\ 1 \\ -3 \\ 4 \\ 100 \end{array} $	1 -1 -1 1 2 -2 -100	-100

change upon electronic excitation, and the modes which
engage motions of the amino group. Strong mixing is predicted
to occur between some out-of-plane modes (see $b_1 \times b_1$ and
$a_2 \times a_2$ submatrices) as well as between in-plane modes of b_2
symmetry.

 $(-NDH \text{ and } -ND_2)$ forms are compared with the vibrational frequencies calculated using the CIS/6-31++G** method for these three isotopic species.

In Table 5 the fundamental frequencies identified in the LIF excitation spectra of 3,5-DCA in native and deuterated

The LIF excitation spectrum of 3,5-DCA allows for assignment of 9 normal vibrations of the a_1 symmetry. The remarkable feature of the ${}^1A_0 \rightarrow {}^1B_2$ LIF excitation spectra of 3,5-DCA is vibronic activity of the vibrational modes which

Table 5Assignments and correlations of the fundamental vibrational frequencies observed in the LIF excitation spectra of 3,5-DCA($-NH_2$), 3,5-DCA(-NDH) and 3,5-DCA($-ND_2$) based on the results of *ab initio* CIS/6-31++G** calculations for the vibrational frequencies and displacements of normal coordinates. The calculated vibrational frequencies are numbered according to increasing frequencies in each electronic state and isotopic species

OIG	10 21	· · · · · · · · · · · · · · · · · · ·
1.5	/ 6- 11	$++(1)^{++}$

c		No			$ar{ u}_{ m scaled}/ m cn$	n^{-1}		$\bar{\nu}_{\mathrm{LIF}}/\mathrm{cm}^{-1}$			$100I/I_0^0$		
S ₀ Nr	C_{2v}	H_2	HD	D_2	$-NH_2$	-NHD	$-ND_2$	-NH ₂	-NHD	$-ND_2$	H_2	HD	D ₂
2	a ₁	3	3	3	115.2	115.1	115.0	110.7	110.5	110.5	19	20	17
9		12	12	12	444.5	444.4	444.4	446.1	445.9	446.0	62	65	63
13		17	17	17	531.4	530.8	530.6	517.6	509.2	506.3	19	21	15
14		14	14	14	521.1	513.4	505.8	508.5	506.4	503.8	32	37	35
23		23	24	24	939.4	940.2	934.7	956.5	958.0	960.3	43	51	49
24		24	25	25	971.5	971.3	963.7	946.9		944.3	13		11
27		27	27	27	1170.7	1157.4	1120.8	1173.2			9		
30		30	30	31	1335.7	1332.0	1343.7	1312.0			3		
31		31	31	32	1404.1	1383.1	1435.9	1390.3		1423.7	25		29
33		34	33	35	1545.3	1494.2	1556.0						
35		35	34	29	1643.4	1528.0	1214.6						
37		37	37	37	2289.2	2289.2	2289.2						
39		39	40	41	3017.4	3017.4	3017.4						
40		40	41	42	3018.9	3018.9	3018.9						
41		41	38	38	3393.1	2545.5	2476.1						
1	b1	2	2	2	94.4	93.6	92.8						
5		5	5	5	177.1	174.6	172.0						
10		13	13	13	479.1	474.0	470.0						
12		7	7	7	293.7	244.9	231.4	I_0^2 904.1	757.0	672.5	28	29	46
16		15	15	16	510.9	510.4	510.5	527.0		527.5	2		9
18		8	8	10	340.3	339.9	340.1						
19		20	20	20	669.7	669.7	669.7						
21		22	22	22	868.5	868.5	868.5						
3	a ₂	1	1	1	81.3	80.9	80.4						
6		10	10	8	370.9	347.4	286.2						
8		6	6	6	199.4	198.6	197.8	226.1	224.2	222.5	6		5
17		16	16	15	516.9	514.2	508.9	520.4	513.8	509.2	25		23
22		18	18	18	596.0	580.2	566.3						
4	b ₂	4	4	4	167.7	165.4	163.2						
7		9	9	9	368.8	351.0	336.4	372.6		357.4			1
11		11	11	11	396.1	394.8	394.1	375.6	374.6	373.5	7		6
15		19	19	19	618.2	612.5	606.7						
20		21	21	23	879.2	851.9	897.6						
25		25	23	21	977.2	906.6	817.0	941.6	831.7	719.4	28		34
26		26	26	26	1096.5	1085.1	1083.8						
28		33	35	34	1525.7	1566.1	1522.1						
29		29	29	30	1289.7	1276.8	1278.0						
32		32	32	33	1444.1	1443.5	1443.3						
34		28	28	28	1225.8	1184.8	1172.6						
36		36	36	36	2263.2	2263.1	2263.1						
38		38	39	40	3014.0	3014.0	3014.0						
42		42	42	39	3508.8	3455.5	2623.7						

involve the aromatic ring. Similar ring mode activities have been found for 3-cyanoaniline.²¹

There are eight other frequencies 226 (a₂), 373 (b₂), 376 (b₂), 520 (a₂), 904 (b₁)², 942 (b₂), 1123 cm⁻¹, and probably 195, 527 (b₁) cm⁻¹ which should be assigned to modes of other symmetry species or their overtones. The electronic excited states of the 3,5-DCA molecule of the C_{2V} symmetry belong to B₂($\pi\pi^*$), A₁($\pi\pi^*$), B₁($\pi\pi^*$) and A₁($\sigma\pi^*/\pi\sigma^*$) irreducible representations. The vibronic coupling of the lowest excited B₂ state can be effective due to b₂ vibrational modes–coupling with A₂ states, a₂ vibrational modes–coupling with B₁ states, and b₁ vibrational modes can give vibronic coupling of the B₂ state with higher ($\pi\pi^*$) excited states of the same B₂ symmetry.

However, since UV absorption spectra show that the higher excited states characterized by a large oscillator strength occur at energies higher than 1 eV above the S_1 state, the vibronic coupling should be of secondary importance for the intensity distribution in the $S_0 \rightarrow S_1$ excitation spectra. Evaluation of S_2 - S_1 vertical energy gaps has been done using CIS/6-31++G** calculation for S_1 excited state geometry and TD B3LYP/6-31++G** calculation for S_0 geometry. These evaluations predict 0.93 eV using TD B3LYP method and 0.63 eV from CIS calculation.

Characteristic features of the LIF excitation spectra of aniline and its derivatives are vibronic transitions involving the inversion mode due to the amino group. The fundamental transition I_0^1 involving one quantum excitation in the inversion mode in the upper electronic state is forbidden. Significant intensity is observed for the overtone transition I_0^2 . One should note here that the forbideness of the I_0^1 transition and the allowance of the I_0^2 transition indicates that: (1) these molecules have bipyramidal structure and (2) the potential energy functions in the ground and excited states being symmetrical relative to the molecular plane are very different and anharmonic. Two vibrational transitions in the LIF excitation spectra: 904 and 942 cm⁻¹ significantly change their frequencies upon exchange of the hydrogen atoms in the amino group on the deuterium atoms, 672 and 719 cm⁻¹ respectively. The first band is a possible candidate for the I_0^2 transition involving inversion motion (b₁ symmetry species) and the second may correspond to the in-plane NH₂ asymmetric bending mode (b₂). The value 904 cm⁻¹ is higher than the I_0^2 transitions in the S₁ state of mono-cyanoanilines (807 cm⁻¹ for 4-cyanoaniline^{13,18} and 833, 855 cm⁻¹ for 2- and 3-cyanoaniline, respectively.²¹ The above seems to indicate that the presence of two cyano groups in the molecule causes further increase of the amino group I_0^2 transition frequency in the S₁ state in comparison to aniline.

The deuterated form (ND₂) spectrum reveals a line splitting due to Fermi resonance between modes 6a 446 cm⁻¹ and 16a² 2×222.5 cm⁻¹. Similar line splitting is not present in other isotopomers because of larger energy difference between 446 and 2×226 cm⁻¹. The mode 16a belongs to the a₂ representation and a significant mixing between this mode and the 10a mode upon electronic excitation is observed. The corresponding off-diagonal coefficients equal 0.50 and -0.52, respectively (see Table 5).

The vector Δq representing the geometry change between the ground state and the excited states and the mode patterns for the totally symmetric normal vibrations (C_{2v}) identified in the LIF excitation spectra of 3,5-DCA are shown in Fig. 5. The displacements of the normal coordinates for the ground state vibrations between the ground state and the excited state are given as the products (projections) of the normal coordinates into vector Δq (see eqn. (A3))

The displacements K for the normal modes are given in Table 6 for 3,5-DCA $(-NH_2)$ and 3,5-DCA $(-ND_2)$ species.

4. Intensities in the LIF excitation spectra of 3,5-dicyanoaniline

The LIF excitation spectra were measured in narrow $\approx 250-300 \text{ cm}^{-1}$ overlapping ($\approx 50 \text{ cm}^{-1}$) spectral ranges. The overlap ranges were used to normalize the spectra. This procedure have been applied repeatedly to calculate the whole excitation spectrum. It is estimated that the relative band intensities are subject to error from about 5% at low wavenumbers to 20% in the upper range of the spectrum.

The intensities of the vibrational bands involving the totally symmetric vibrational modes in the LIF excitation spectrum of 3,5-DCA have been calculated using multimode Franck-Condon overlap integrals. For this purpose the ab initio results for the displacement of the normal modes, the vibrational frequencies and Dushinsky rotation matrices have been applied. The recurrence formulae derived by Ruhoff^{31,32} have been used for the intensity calculation. The equations are presented in Appendix B. Table I (ESI) in column 7 gives the predicted relative band intensities using the molecular geometries and the normal modes derived from the HF/6-31++G** calculation for the ground electronic state and the CIS/6-31++ G^{**} calculation for the lowest excited electronic state of 3,5-DCA. In this calculation the Dushinsky rotation matrix, displacement parameters K from Table 4 and unscaled vibrational frequencies have been used. Moreover, all totally symmetric vibrational modes have been taken into account. From Table 4 it is evident that five vibrational modes with K_i greater than 0.1 give major contribution to the LIF excitation spectrum. These dominant modes are shown in Fig. 3. The corresponding mode patterns for the ground state S_0 (planar geometry) and excited S₁ state for these dominant modes are drawn. The results of the modeling of the intensity distributions in the LIF excitation spectra are presented in Fig. 4.

The multidimensional vector Δq representing geometry change upon electronic excitation derived from the ab initio quantum mechanical calculation is shown in Fig. 5a. To visualize the geometry change in Fig. 5a the coordinates representing Cartesian displacements of the atoms have been multiplied by a constant factor of 40. The result is shown in Fig. 5a. Comparing the data in Table I of the ESI,† e.g. the column 6 (containing the observed relative intensities) and the column 7 (showing the calculated relative intensities based on the ab initio results) we find that there is a remarkable degree of correlation between the observed and calculated band intensities. It should be noticed that in this modeling of the intensity distributions we have neglected a possible role of the totally symmetric modes as the modes engaged in the vibronic coupling between the lowest excited state and higher excited electronic states of the B₂ symmetry.

The predictions of the relative intensity can be even improved using optimization procedures. In this approach the intensity distribution in the LIF excitation spectrum was calculated using the *ab initio* results except of the displacement parameters which were fitted to get the intensities as close as possible to the observed ones. In the last column 8 in Table I (ESI[†]) the results of this particular calculation is shown, as well as in Fig. 4, where intensities from LIF spectrum, *ab initio* parameters and fit are compared.

Knowing the displacement parameters for the totally symmetric vibrational modes from the fitting and the normal mode coordinates from the ab initio quantum mechanical calculations, the vectors Δq have been calculated using eqn. (A6) given in Appendix A. The resultant geometry transformations for the $S_0 \rightarrow S_1$ excitation are shown in Fig 5c and d. These geometry changes have been derived from the LIF excitation spectra of the 3,5-DCA(-NH₂) and 3,5-DCA(-ND₂) forms, respectively. The geometry transformations shown in Fig. 5a and 5c,d are close to each other. The changes in the benzene ring geometry shown in Fig. 5a and 5c,d are the same. The main difference in geometry change predicted by these two approaches is seen for the substituent groups. The displacement vectors derived from the optimization procedure for 3,5-DCA(-NH₂) molecule and 3,5-DCA(-ND₂) molecule are shown in Table 6.

5. Summary

LIF excitation spectra of jet-cooled 3,5-DCA molecules in native and deuterated forms have been investigated. The

Table 6 Normal mode displacements for a_1 vibrations of the planar3,5-DCA molecule, from *ab initio* calculations and from the intensitydistribution

G 1	3,5-DCA(-)	NH ₂)	3,5-DCA(-ND ₂)			
S ₀ pl No	$\overline{K_i}$	K_i^{fit}	$\overline{K_i}$	K_i^{fit}		
2	-0.249	-0.288	0.249	0.277		
10	0.254	0.313	-0.254	-0.353		
13	-0.066	-0.177	0.194	0.068		
14	0.220	0.145	-0.126	-0.229		
23	0.137	0.164	-0.111	-0.201		
24	0.052	0.079	-0.102	-0.053		
28	-0.043	-0.067	-0.017	-0.007		
30	-0.124	-0.099	0.110	0.093		
31	-0.040	-0.043	0.045	0.044		
33	-0.015	-0.002	0.010	0.024		
35	0.008	0.013	0.075	0.113		
37	0.023	-0.031	-0.023	-0.004		
39	-0.007	-0.007	0.007	-0.004		
40	0.000	-0.000	0.000	0.000		
41	0.007	0.009	-0.031	-0.039		



Fig. 3 Mode patterns of the normal vibrations of planar 3,5-DCA molecule in its S_0 and S_1 electronic states. Selected modes give major contribution to the LIF excitation spectra of 3,5-DCA.

ground state vibrations of 3,5-DCA in crystalline state have been studied using IR and Raman spectroscopic techniques. The *ab initio* HF and CIS calculations of vibrational frequencies have been performed for 2,6-dicyanoaniline in the S₀ and S₁ electronic states using the $6-31++G^{**}$ basis set. The correlations between calculated and measured vibration frequencies have been proposed for the ground electronic state and the first excited singlet state S₁ (¹B₂ symmetry). It has been found that the dominant vibronic bands in the excitation spectra are connected with the modes involving in-plane motions of 3,5-DCA. The intensity distributions in the LIF excitation spectra of 3,5-DCA were modeled. A qualitative agreement between measured and calculated intensities have been reached for the majority of totally symmetric fundamentals.

The assignments of the I_0^2 transition in the LIF excitation spectra of 3,5-DCA and its deuterated derivatives have been proposed (904 cm⁻¹/672 cm⁻¹). It has been found that the frequencies of the I_0^2 bands increase with the number of cyano substituents in the aniline molecule. The transition I_0^2 involving inversion motion of the amino group in 3,5-DCA



Fig. 4 Intensity distribution: peaks of a_1 and b_1 symmetry. a) from the LIF spectrum of 3,5-DCA($-NH_2$); b) modeling: parameters from *ab initio* calculations; c) modeling: K_i fitted to reproduce experimental intensities (see text for details).

has significant intensity. This latter property is a consequence of large change in the potential function between the A_1 ground state (double minimum) and the B_2 excited electronic state (single minimum) for the inversion coordinate of the amino-group.

Remarkable features of the¹B₂ LIF excitation spectra of jet-cooled 3,5-DCA are vibronic activities of these vibrational modes which involve aromatic ring motion mode No 12 = 6a, No 14 = 7a and No 23 = 1. The similar ring modes activity have been found earlier for other cyanoanilines: 2,6-dicyanoaniline^{21,23} and 3-cyanoaniline. Moreover, it has been found that the LIF excitation spectrum for deuterated form of 3,5-DCA(-ND₂), reveals a line splitting due to Fermi resonance between 6a 446 cm⁻¹ and $16a^2 2 \times 222.5$ cm⁻¹ modes.

The important difference between *ortho-* and *meta-substi*tuted cyano derivatives of aniline: 3,5-DCA and 3-cyanoaniline *versus* 2,6-DCA and 2-cyanoaniline, is a small intensity of the band corresponding to the in-plane motion of the cyano group (C-CN bending, 9a in 3,5-DCA) in meta- substituted compounds.

It is generally assumed that the predictions concerning the molecular structure and the vibrational motions in the excited electronic states reveal distinct deficiency of the CIS method. This is due to insufficient evaluation of the electron





Phys. Chem. Chem. Phys., 2003, 5, 4096–4107 4105

correlations when the configuration interaction is limited to singly excited configurations. In particular the electronic excitation energies are considerably overestimated. For the 3,5-DCA molecule, the predicted intensities in LIF excitation spectra for some totally symmetric vibrations 12 and 23 are underestimated. In conclusion, it seems that the CIS/ $6-31++G^{**}$ calculation underestimates the changes of molecular geometry accompanying the $S_0(A_1) \rightarrow S_1(B_2)$ electronic transition in the 3,5-DCA molecule.

Present study clearly shows that for the vacuum-isolated jet-cooled 3,5-DCA molecule where intramolecular hydrogen bonding is unimportant the substituants of the benzene ring undergo smaller geometry change than in 2,6-DCA. This conclusion is well reproduced by the results of the *ab initio* calculation shown in Fig. 5a and 5b as well as by the observed intensities of the in-plane bending vibrations of the cyano groups in the LIF excitation spectra shown in Fig. 4. and reported in ref. 23.

Appendix A

Normal mode coordinates for the ground state (g) and excited state (e) are linear combinations of mass weighted displacements of the Cartesian coordinates from equilibrium geometry in the corresponding electronic state, g or e:

$$Q_j^{\rm g(c)} = \sum_{k=1}^{3N} l_{jk}^{\rm g(c)} (q_k - q_k^{\rm g(c)}) \tag{A1}$$

where Q_i are the normal mode coordinates and q_k are the mass weighted Cartesian coordinates of the atoms. In eqn. (A1) the equilibrium geometries of the molecule are described by the set of mass weighted Cartesian coordinates $\{q^x\}$ where x = g or e. Normal coordinates in the two electronic states are related as follows:

$$\boldsymbol{Q}^{\mathrm{e}} = \boldsymbol{D} + \boldsymbol{R}\boldsymbol{Q}^{\mathrm{g}} \tag{A2a}$$

$$\boldsymbol{Q}^{\mathrm{g}} = \boldsymbol{K} + \boldsymbol{J}\boldsymbol{Q}^{\mathrm{e}} \tag{A2b}$$

where the components D_j and K_j of the displacement vectors of the normal modes **D** and **K** are given by

$$D_i = \sum_{k=1}^{3N} l_{ik}^{\mathrm{e}} (q_k^{\mathrm{e}} - q_k^{\mathrm{g}})$$

and

$$K_{i} = \sum_{k=1}^{3N} l_{ik}^{g} (q_{k}^{e} - q_{k}^{g})$$
(A3)

whereas the elements R_{ij} and J_{jj} of the rotation matrices **R** and **J** are given by

 $R_{ij} = \sum_{k=1}^{3N} l_{ik}^{\mathrm{e}} (l^{\mathrm{gT}})_{kj}$

and

$$J_{ij} = \sum_{k=1}^{3N} l^g_{ik} (l^{eT})_{kj}$$
(A4)

respectively. The rotation matrix gives a useful measure of normal modes correlation, and their mixing upon isotopic exchange or electronic excitation. This approach is correct within harmonic approximation for potential energy functions. The matrix elements of the Dushinsky R_{ij} matrix represent projections of normal coordinates in the ground electronic state on normal mode coordinates in the S₁ excited state. On the other hand, the components of the displacement vector D_i represents the projections of the normal coordinates for the excited state onto the vector Δq : $\Delta q_k = q_k^e - q_k^g$, where k = 1, ..., 3N. The vector Δq describes the geometry change

upon electronic excitation in the mass weighted Cartesian coordinates. The components of the displacement vector, K_i , represent the projections of the normal coordinates for the ground state onto the same vector Δq .

The geometric transformation has been performed as follows:

Since from eqn. (A3) the following relation holds

$$K = l^{g} \cdot \Delta q$$

we find

$$\Delta \boldsymbol{q} = \boldsymbol{l}^{\mathrm{gT}} \cdot \boldsymbol{K} \tag{A5}$$

and in Cartesian coordinates we have the following relation

$$\Delta \xi = \boldsymbol{I}_{\text{cart}}^{\text{gT}} \cdot \boldsymbol{K} \tag{A6}$$

Output from the Gaussian98 program ²⁷ contains the Cartesian normal mode coordinates, which are defined as $l_{ik}^{\text{cart}} = l_{ik}/\sqrt{m_k}$. From these coordinates, components of the l_{ik} were recovered by multiplying l_{ik}^{cart} by $\sqrt{m_k}$. The resultant $l \cdot l^{\text{T}}$ matrix was orthogonal and normalized as required.²⁷ Dimensionless displacements for normal mode coordinates x_i were derived using calculated mode frequencies as: $x_i = D_i \sqrt{2\pi\nu_i}/\hbar$.

Appendix **B**

Let consider a simple case where the normal coordinates in the two electronic states are related by the relation (A2b). The multidimensional overlap integrals are defined by general relations.^{31,32}

$$I(\boldsymbol{n}^{q}; \boldsymbol{n}^{e}) = N \int \psi^{g}(\boldsymbol{n}^{g}) \psi^{e}(\boldsymbol{n}^{e}) \mathrm{d}\boldsymbol{Q}^{e}$$
(B1)

where $N = (\det J)^{-1/2}$. In more direct form they are given by

$$I(\mathbf{n}^{g}; \mathbf{n}^{e}) = C \int \exp[-(\mathbf{Q}^{g\dagger} \boldsymbol{\Gamma}^{g} \mathbf{Q}^{g} + \mathbf{Q}^{e\dagger} \boldsymbol{\Gamma}^{e} \mathbf{Q}^{e})/2] \\ \times \boldsymbol{H}_{\mathbf{n}^{g}}(\boldsymbol{\Gamma}^{g1/2} \mathbf{Q}^{g}) \boldsymbol{H}_{\mathbf{n}^{e}}(\boldsymbol{\Gamma}^{e1/2} \mathbf{Q}^{e}) \mathrm{d} \mathbf{Q}^{e}$$
(B2)

In the present calculations of the fluorescence excitation spectrum we have used diagonal matrices of the corresponding vibrational frequencies

$$\boldsymbol{\Gamma}^{g} = \begin{pmatrix} \omega_{1}^{g} & 0 & 0\\ 0 & \omega_{2}^{g} & 0\\ 0 & 0 & \ddots \end{pmatrix}, \boldsymbol{\Gamma}^{e} = \begin{pmatrix} \omega_{1}^{e} & 0 & 0\\ 0 & \omega_{2}^{e} & 0\\ 0 & 0 & \ddots \end{pmatrix}$$
(B3)

The multidimensional Franck–Condon overlap integrals were calculated using the recursion relations given by Ruhoff ³¹ for the transitions from the lowest vibrational state. The Franck–Condon factors of the assigned transitions were calculated as squares of the Franck–Condon overlap integrals, *i.e.*, $|I(0;n^e)|^2$. The corresponding overlap integrals are given in terms of the J, Γ^g and Γ^e matrices using the following definitions:

$$S = J^{+} \Gamma^{g} J + \Gamma^{e}, C = 2\Gamma^{e1/2} S^{-1} \Gamma^{e1/2} - 1 \text{ and}$$
$$X = -2 \Gamma^{e1/2} S^{-1} J^{+} \Gamma^{g} K$$
(B4)

Relative probabilities for transitions starting in the ground vibrational level are evaluated as

$$I(\mathbf{0}^{\rm g}; \mathbf{n}^{\rm e})|^2 / |I(\mathbf{0}^{\rm g}; \mathbf{0}^{\rm e})|^2$$
 (B5)

where the overlap integral $I(0^{g}; 0^{e})$ is given by

$$I(\mathbf{0}^{g}, 0, 0, \dots, 0) = \left(\frac{2^{\alpha} \det(\boldsymbol{\Gamma}^{g} \boldsymbol{\Gamma}^{e})^{1/2}}{\det(\boldsymbol{J}\boldsymbol{S})}\right)^{1/2} \\ \times \exp\left(\frac{1}{2}\boldsymbol{K}^{\dagger}[\boldsymbol{\Gamma}^{g} \boldsymbol{J}\boldsymbol{S}^{-1}\boldsymbol{J}^{\dagger} - 1]\boldsymbol{\Gamma}^{g}\boldsymbol{K}\right) \quad (B6)$$

and the overlap integrals $I(0^{g}; n^{e})$ are calculated using the recursion formula

$$I(\mathbf{0}^{g}, 0, \dots, 0, n_{m}, \dots, n_{\alpha}) = \frac{1}{(2n_{m})^{1/2}} [X_{m}(I(n_{m}-1) + (2(n_{m}-1))^{1/2}C_{mm}I(n_{m}-2) + \sum_{k=m+1}^{\alpha} \left(\frac{n_{k}}{2}\right)^{1/2}(C_{mk} + C_{km}) \times I(n_{m}-1, n_{k}-1)]$$
(B7)

The eqns. (B5)-(B7) are sufficient for calculation of the intensity distribution of the vibronic transitions in the LIF excitation spectra of jet-cooled molecules.

Acknowledgements

This work was supported by grants from the Polish State Committee for Scientific Research 3T09A 086 16 and KBN/SGI ORIGIN 2800/UJ/026/1999 and the grants of the Academic Computer Center. The authors thank Prof. Janusz Sepioł for his suggestions concerning synthesis of cyanoanilines and Dr A. Birczyńska-Wesełucha, Ms M. Jakus and Ms T. Szpyt for measuring Raman and IR spectra. We thank also referee for his valuable comments.

References

- G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand Reinhold Company, New York, 1966.
- K. G. Spears and S. A. Rice, J. Chem. Phys., 1971, 55, 2 5561
- 3 L. Goodman and R. P. Rava, Adv. Chem. Phys., 1983, 54, 177.
- A. E. W. Knight, C. S. Parmenter and M. W. Schuyler, J. Am. 4 Chem. Soc., 1975, 1993, 97, 2005.
- G. Orlandi, P. Palmieri, R. Tarroni, F. Zerbetto and M. Z. Zgierski, J. Chem. Phys., 1994, 100, 2458. K. Y. Tang and C. S. Parmenter, J. Chem. Phys., 1983, 78,
- 6 3922.
- 7 Birks, Photophysics of Aromatic Molecules, Wiley-IB Interscience, London, 1970.
- 8 M.Stockburger, in Organic Molecular Photophysics, ed. J.B.Birks, Wiley-Interscience, London, 1973, vol. 1, p. 57-102.
- R. D. Gordon, D. Clark, J. Crowley and R. Mitchell, Spectrochim. Acta, Part A, 1984, 40, 657.
- N. Mikami, A. Hiraya, I. Fujiwara and M. Ito, Chem. Phys. Lett., 10 1980. 74. 531.

- J. M. Hollas, M. R. Howson, T. Ridley and L. Halonen, Chem. 11 Phys. Lett., 1983, 98, 611.
- D. Phillips, J. Photochem. Photobiol. A: Chem., 1997, 105, 307. 12
- 13 S. Wategaonkar and S. Doraiswamy, J. Chem. Phys., 1996, 105, 1786 J. August, T. F. Palmer, J. P. Simons, C. Jouvet and W. Rettig, 14
- Chem. Phys. Lett., 1988, 145, 273. J. Herbich, F. P. Salgado, R. P. H. Rettschnick, Z. R. Grabowski 15
- and H. Wójtowicz, J. Phys. Chem., 1991, 95, 3491. 16
- C. Dedonder-Lardeux, C. Jouvet, S. Martrenchard, D. Solgadi, J. McCombe, B. D. Howells, T. F. Palmer, A. Subaric-Leitis, C. Monte, W. Rettig and P. Zimmermann, *Chem. Phys. Lett.*, 1995, 191, 271.
- 17 A. L. Sobolewski and W. Domcke, Chem. Phys. Lett., 1996, 259, 119.
- 18 E. M. Gibson, A. C. Jones and D. Phillips, Chem. Phys. Lett., 1988. 146. 270.
- 19 H. Yu, E. Joslin, B. Crystall, T. Smith, W. Sinclair and D. Phillips, J. Phys. Chem., 1993, 97, 8146.
- 20 R. Howell, E. M. Joslin, A. G. Taylor and D. Phillips, J. Chem. Soc., Faraday Trans., 1992, 88, 1605.
- 21 P. Kolek, K. Pirowska and J. Najbar, Phys. Chem. Chem. Phys., 2001, 3, 4874.
- W. Roth, P. Imhof and K. Kleinermanns, Phys. Chem. Chem. 22 Phys., 2001, 3, 1806.
- 23 P. Kolek, K. Pirowska, M. Góra, B. Kozik and J. Najbar, Chem.-Phys., 2002, 285, 55.
- P. Kolek, P. Gajdek, K. Pirowska and J. Najbar, J. Mol. Struct., 24 1999, 511/512, 117; D. T. Mowry, Chem. Rev., 1948, 42, 189-283.
- 25 D. T. Mowry, Chem. Rev., 1948, 42, 189-283.
- 26
- H. J. Barber and R. Slack, *J. Chem. Soc.*, 1947, 82. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUS*-SIAN 98 (Revision A.9), Gaussian, Inc., Pittsburgh, PA, 1998.
- J. B. Foresman, M. Head-Gordon, J. A. Pople and M. J. Frisch, 28 J. Phys. Chem., 1992, 96, 135.
- 29 H. Yoshida, A. Ehara and H. Matsuura, Chem. Phys. Lett., 2000, 325 477
- 30 G. Varsanyi, Assignments of Vibrational Spectra of 700 Benzene Derivatives, Akademiai Kiado, Budapest, 1973.
- 31 P. T. Ruhoff, Chem. Phys., 1994, 186, 355-374.
- T. E. Sharp and H. M. Rosenstock, J. Chem. Phys., 1964, 41, 32 3453.