

Terahertz spectroscopy of dicyanobenzenes: Anomalous absorption intensities and spectral calculations

O. Esenturk¹, A. Evans², E.J. Heilweil^{*}

Optical Technology Division, Physics Laboratory, National Institute of Standards and Technology, 100 Bureau Drive Mailstop 8443, Gaithersburg, MD 20899-8443, USA

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Abstract

Terahertz absorption spectra of three isomeric structures of dicyanobenzene in chloroform solution and solid phase at 298 K are reported. These spectra exhibit enhanced absorption in low THz range compared to most organic systems because of strong coupling to phonon modes. Molecular vibrational spectral calculations show strong correlation with the experiment especially for solution spectra. All intramolecular modes were assigned and intermolecular modes identified. Out-of-plane intramolecular modes at low frequency exhibit $\sim 75 \text{ cm}^{-1}$ blue shifts as the secondary CN group moves from the para to ortho position on the benzene ring, whereas almost no frequency shift occurs for low-frequency in-plane modes.

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1. Introduction

Vibrational spectroscopy and mode assignment investigations of the dicyanobenzene (DCB) isomers were previously conducted by several groups [1–5] but little attention was paid to the low frequency Terahertz (THz) region of the spectrum. The reported infrared studies are sparse and often inconsistent, especially in THz frequency region, because of difficulties in spectrally accessing this region with conventional FTIR spectrometers. Higgins et al. have reported calculated low frequency internal modes of the isomers [1]. However, our attempt to reproduce their calculated frequencies using their reported structural parameters and basis set with GAUSSIAN 03 W

software package failed thus prompting us to redo the spectral calculation for all three isomers. In addition, because of the DCB isomers' planar structures and weakly interacting nature in the solid state [6–9], investigation of the DCB isomers provides an excellent example with which to compare experiment and current theory. The theoretical calculations can be performed with commercially available and cost-effective Density Functional Theory (DFT) software packages instead of highly expensive solid-state calculations. These DFT packages have been used reliably for mid-IR spectroscopic investigations of molecules for many years and have recently been applied to low frequency molecular calculations [10–13]. In addition, the DCB isomers have strongly coupled electro-negative cyano groups connected to the pi-bonded benzene ring, which affords the possibility that partial atomic charges undergoing vibrational dipolar motions could enhance THz absorption intensities making comparison to theory straightforward. Many of these experimental and theoretical characteristics were borne out and are reported in this Letter.

We investigated the vibrational motions of DCBs in the solid state by concentrating on the spectral region between 10 cm^{-1} and 700 cm^{-1} , especially below 250 cm^{-1} , where

^{*} Corresponding author. Fax: +1 301 975 6991.

E-mail address: edwin.heilweil@nist.gov (E.J. Heilweil).

¹ Optical Technology Division, NIST Guest Researcher. Present address: Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA.

² High School student, Charles E. Smith Jewish Day School, Rockville, MD 20852. Present address: Department of Electrical Engineering, Cornell University, Ithaca, NY 14850, USA.

crystal lattice phonon vibrations and internal molecular modes occur. 1,2-, 1,3- and 1,4-isomers of dicyanobenzene differ only by the ring location of their two-cyano groups, yet they exhibit significantly different vibrational spectra. These differences are due primarily to the slight structural variations of these molecules coupled with variations in their crystal lattice structures. Intermolecular modes of the isomers were identified with the help of calculations and comparison to solution spectra where these modes are eliminated. To our knowledge, this study represents the first unified theoretical broad bandwidth spectral comparison between the internal and external modes measured by both THz-time domain spectroscopy and far-IR Fourier transformed infrared experiments for all three DCB isomers.

2. Experimental

1,2-, 1,3- and 1,4-dicyanobenzene isomers (98% purity) were purchased from the Sigma–Aldrich Company and used as is.³ Polyethylene (PE) powder (MicroPowders Inc.) is used as a transparent matrix for crushed DCB solid pellet samples. It has less than 10 μm mean particle size (much smaller than the applied THz optical frequencies) thus eliminating possible etalon interference and scattering effects in the THz spectra. Solid samples were prepared by mixing 5 mg of sample with ~ 95 mg PE and pressed as a pellet in a 13 mm diameter vacuum die at the lowest possible pressures (ca. 200 psi or 1.4×10^6 Pa) to minimize decomposition due to pressure and transient heating. The optical density (OD) of the samples was obtained by ratioing the raw sample transmission spectra (T_{sample}) to that of a pressed 100 mg polyethylene blank (T_{PE}) disk ($\text{OD} = -\log_{10}(T_{\text{sample}}/T_{\text{PE}})$) (512 averaged spectral scans under 60 min purged dry-air). Similarly, liquid-phase spectra were collected using 0.16 M solutions of each DCB isomer dissolved in chloroform using a 1.2 mm path-length cell with polished 3 mm thick high resistivity silicon windows and background corrected against a blank chloroform sample. FTIR spectra were acquired using a Nicolet 550 Magna-IR Series II spectrometer modified with a silicon-coated broadband beam-splitter and a deuterated triglycine sulfate (DTGS) room temperature detector fitted with a transparent high-density polyethylene window.

The THz time-domain spectroscopy (THz-TDS) technique was used to collect spectra of the same species between 10 cm^{-1} and 225 cm^{-1} for solid pellet and 10 cm^{-1} – 90 cm^{-1} for liquid samples. The THz-TDS approach typically uses a common apparatus, and a review of the technique and experimental set-up are reported elsewhere [14]. In our apparatus, matching 0.150 mm GaP

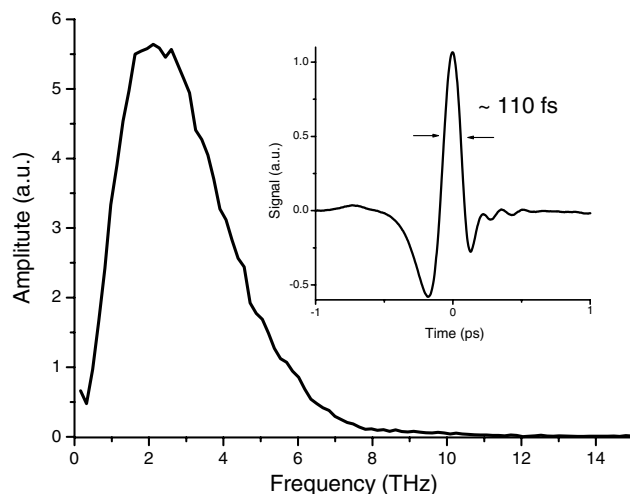


Fig. 1. Frequency domain spectrum of free-space propagating THz pulses using 0.15 mm thick GaP generation and detection crystals showing the resultant THz-TDS bandwidth. The inset depicts a typically acquired time-domain waveform of these pulses.

(110) difference-frequency mixing crystals for THz generation and electro-optic detection of THz pulses with ~ 200 nJ gate 800 nm pulses extended the typical 0.3–3 THz spectral bandwidth to >8 THz of our instrument (Fig. 1). Similar to FTIR measurements described above, the raw sample spectra are corrected by using a PE background spectrum to obtain sample absorption spectra. FTIR and THz-TDS spectra were collected after purging each instrument with dried air to remove water vapor interference. Analysis for comparison of averaged spectra (512 scans for FTIR and 20 for THz-TDS measurements) to theory yielded an intensity uncertainty from the baseline of less than ± 0.005 optical density (OD) units ($k = 1$; type B analysis).

Density functional geometry optimizations and vibrational frequency calculations of the DCB isomers were performed by GAUSSIAN software (G03W Rev B.02) [15] with the Becke-3-Lee–Yang–Parr (B3LYP) functional and 6-311++G* basis set on a Pentium 4/2 GB desktop under the Windows 32 environment. The resulting non-negative vibrational frequencies and close agreement to bond lengths and angles ($<1\%$ deviation) with published crystallographic data for these systems [6–9] confirmed that the calculated minimized structures of the molecules were obtained (Fig. 2).

3. Results and discussion

3.1. 1,2-Dicyanobenzene

The upper panel of Fig. 3 compares the experimental and calculated THz vibrational spectra of 1,2-DCB. All four spectra agree well throughout the reported spectral range. Minor frequency red shifts for features below 250 cm^{-1} and blue shifts for the features above 350 cm^{-1} are observed in the gas phase calculations relative to solid

³ Certain commercial equipment, instruments, or materials are identified in this Letter to adequately specify the experimental procedure. In no case does identification imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

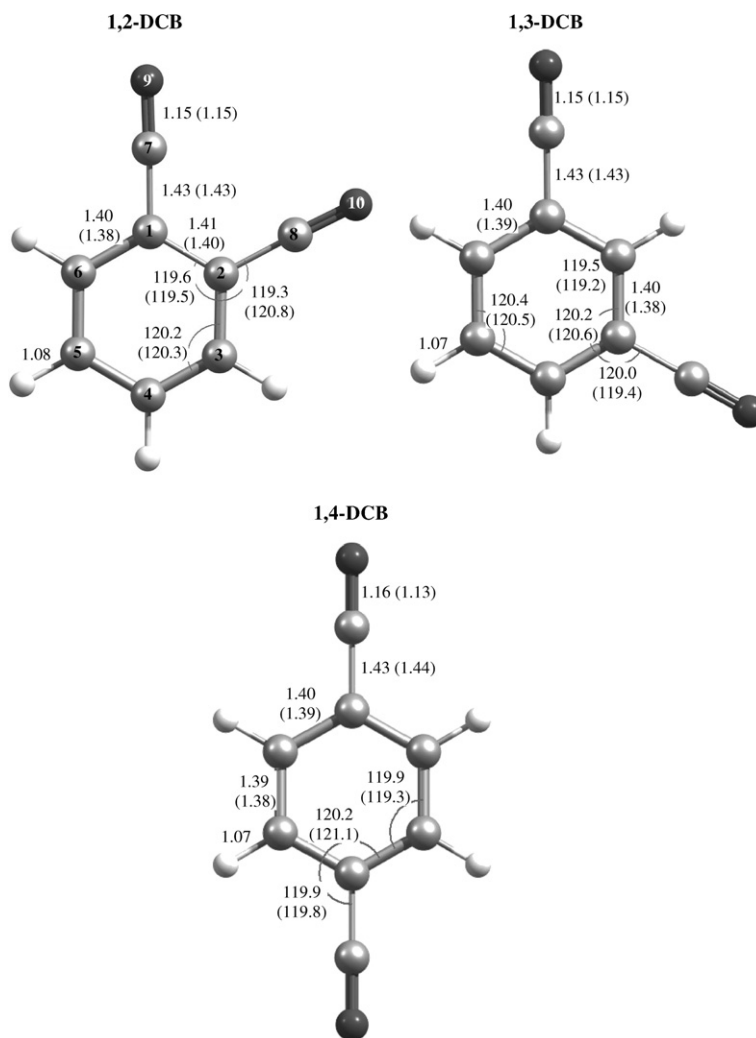


Fig. 2. Optimized gas phase structures of DCB isomers (nitrogen: dark gray, carbon: gray). Selected bond lengths (angstroms) and angles (degrees) are shown along with the reported crystal structure data [6–9] given in parenthesis.

and solution FTIR spectra. The frequency shifts are not consistent or incremental throughout the spectral region; therefore, there is no obvious uniform way for correcting the calculated gas phase spectrum to experiment.

The solid FTIR spectrum of the 1,2-DCB isomer consists of two regions; below 250 cm^{-1} and above 350 cm^{-1} . The higher frequency range contains five significant features (Table 1) and all of these features are observed in the solution-phase spectrum with no significant shifts. In addition, the bandwidths of the features observed in solution are significantly narrower than those in the solid spectrum. Several of the solution phase absorptions appear to have a Lorentzian band shape suggesting the liquid system is homogeneous while the solid spectra do not show this behavior due to inhomogeneous intermolecular broadening effects in the solid.

The lower ($<250\text{ cm}^{-1}$) frequency range of the solid spectrum contains five absorption features (Table 1). Only three of these features (all above 100 cm^{-1}) are found in the solution spectrum. Minor red-shifts ($\leq 6\text{ cm}^{-1}$) occur in the solution spectrum compared to the solid-state features,

which again, probably arises from weak solvent–solute interaction compared to slightly stronger interactions that exist in solid phases such as inhomogeneous broadening caused by dipolar interactions. Both the solution and gas phase spectra portray only three features in this range confirming that the observed two lowest frequency absorption features at 50 cm^{-1} and 73 cm^{-1} in solid samples must arise from intermolecular phonon modes. Lack of any features in the THz solution spectra (d in Fig. 3) confirms this finding. Representations of the three internal mode atomic motions with displacement vectors are given in Fig. 4.

According to the calculations, one of the three internal modes (feature at 177 cm^{-1} in the solid phase spectrum and 169 cm^{-1} in the simulation spectrum) is an out-of-plane mode where the two cyano and the opposite ends (hydrogens) of the molecule bend symmetrically (without deforming the benzene ring) in a butterfly-like motion. Comparison of the relative intensities of these three internal modes in simulation and solution spectra to their counterparts in the solid-state spectrum suggests that the out-of-plane mode intensity is significantly enhanced for

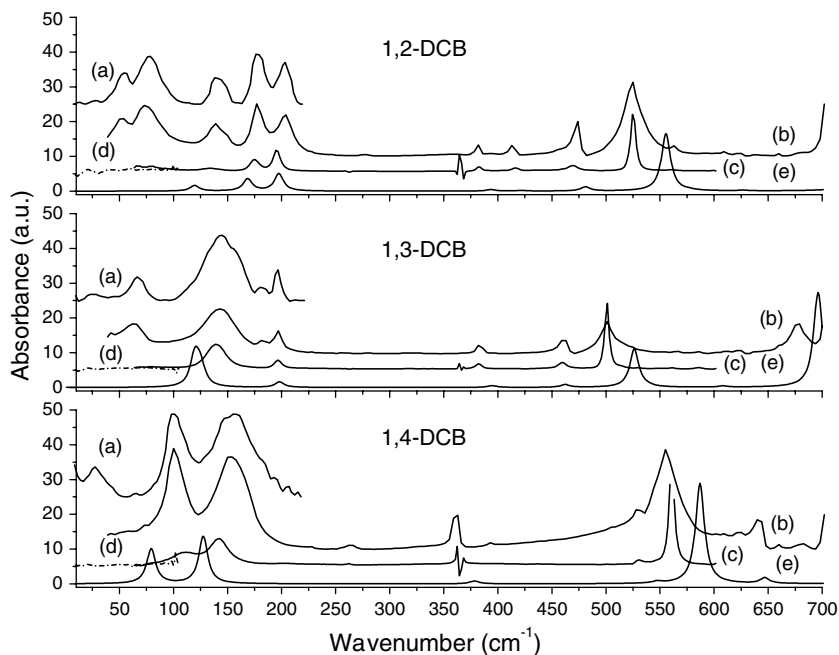


Fig. 3. Experimental and simulation spectra of DCB isomers. Spectra of solid phase in PE matrix measured by (a) THz-TDS and (b) FTIR, of solution phase (in chloroform) measured by (c) FTIR and (d) THz-TDS and (e) DFT simulations. To simplify, solution spectral intensities are multiplied by 10, while the solid THz spectra are scaled by 2. Spectra are vertically offset for clarity. See discussion for extinction coefficients for the isomers.

the crystalline structure. The origin of this enhancement will be discussed in section 4.

3.2. 1,3-Dicyanobenzene

In parallel to the 1,2-isomer, the 1,3-DCB solid, solution and simulated spectra exhibit comparable frequency and intensity correlation, as seen in the middle panel of Fig. 3. Similar minor red and blue shifts between the simulated and experimental spectra are observed. For this isomer, the frequencies and intensities of absorption features observed in the solution-phase spectrum correlate very well with the solid spectrum, exhibiting almost no frequency shift.

As was found for 1,2-DCB, the solid FTIR spectrum of 1,3-DCB portrays both low and high frequency regions. In the high frequency range ($>350\text{ cm}^{-1}$), we observe four absorption features in the solid spectrum, and three of those are also observed in the solution spectrum. One ‘missing’ solid-state feature near 680 cm^{-1} is masked by a strong solvent absorption. Similar to 1,2-DCB, the features in the solution-phase spectrum are significantly narrower than those for the solid spectrum due to limited inhomogeneous broadening.

There are three observed significant features in the low frequency range of the solid FTIR spectrum. The THz-TDS study yields the same low-frequency spectrum but with an additional weak feature at 27 cm^{-1} . Only two of these four solid-state features are observed in the solution and simulation studies. One of the two solution-phase spectral features (at 139 cm^{-1}) is red-shifted by 4 cm^{-1} com-

pared to the solid spectrum. The simulation suggests that the band observed in solution is a combination of two intramolecular modes with intensity ratio of $\sim 1.5:1$. Sharpening of the bandwidths of the observed modes in the solution spectrum will favor a shift toward the lower frequency band and produce a slight red shift compared to the solid spectrum, as is observed. The three lowest simulated IR-active internal modes for 1,3-DCB with displacement vectors are also shown in Fig. 4. Absorption features that are observed in the solid data but not observed in the solution or simulation spectra most likely arise from intermolecular modes of the 1,3-DCB crystal lattice. The intermolecular mode frequencies and intensities are comparable to those observed for the 1,2-isomer. Slight frequency differences probably arise from structural differences; the 1,3- crystal structure has a slightly smaller unit cell volume and closer plane–plane distances compared to those of the 1,2-DCB isomer [7]. In addition, the 1,3-DCB molecules are oriented such that the CN groups of two adjacent molecules oppose each other in the lattice and thus reduce the long-range dipole organization that exists for the 1,2-DCB isomers.

The weak absorption feature observed at 181 cm^{-1} in the solid spectrum does not correspond to any feature in either the solution or simulated spectra. However, the simulation predicts an IR-inactive out-of-plane mode in this frequency region. Perhaps perturbations by strong interaction of phonon modes with this out-of-plane IR-inactive mode may activate it; thereby, resulted in observation of the mode in the solid-state spectrum but not in solution. (See discussion in Section 4.)

Table 1
Calculated and experimental vibrational features for the 1,2-, 1,3- and 1,4-DCB isomers

1,2-DCB (Orthorhombic, $V/Z(2) = 170.4 \text{ \AA}^3$, $d = 1.25 \text{ g/cm}^3$)									
	G03W		FTIR			Thz-TDS		Higgins et al. [1]	
	ν	I	ν_s	ν_l	I	V	I	ν	I
			50		m	54	m		
			73		m	79	m		
A2	112	0.0						109	0.0
A1	119	1.6	139	135	m	144	m	113	1.5
B1	169	3.5	177	175	m	180	m	165	4.0
B2	197	5.0	201	195	m	206	m	185	4.5
A2	378	0.0	278		(v)w			365	0.0
B1	394	0.4	382	382	w			383	1.0
B2	421	0.2	413	416	w			408	0.1
A1	481	1.2	474	469	m			458	0.7
B1	555	16.5	525	525	s			534	13.9
A1	578	0.1	563	561	(v)w			555	0.0
A2	587	0.0						566	0.0
B2	627	0.2						594	0.1
A1	719	2.4						699	2.2
1,3-DCB (Monoclinic, $V/Z(4) = 165.75 \text{ \AA}^3$, $d = 1.28 \text{ g/cm}^3$)									
						27	w		
			62		m	71	m		
A1	120	9.0	143	139	s	147	s	113	7.9
B1	125	5.6						122	5.6
A2	162	0.0	181		w	184	w	157	0.0
B2	198	1.6	197	197	s	201	m	186	1.4
A2	381	0.0						367	0.0
B1	395	0.5	382	382	m			382	1.4
A1	462	0.8	459	459	m			449	0.7
B2	465	0.0						451	0.0
B1	526	11.0	501	502	s			504	10.3
A1	538	0.2						505	0.0
B2	608	0.4						577	0.1
A2	648	0.0						619	0.0
B1	696	27.3	675		m			676	14.3
1,4-DCB (Monoclinic, $V/Z(2) = 164.75 \text{ \AA}^3$, $d = 1.28 \text{ g/cm}^3$) (Triclinic, $V/Z(1) = 166 \text{ \AA}^3$)									
						11	w		
						33	w		
B3u	79	10.0	100	110	s	106	s	77	9.2
B2u	128	13.7	154	143	s	157	s	119	12.0
B3g	196	0.0						183	0.0
B2g	198	0.0	266		w			190	0.0
B3u	378	0.8	363		m			365	2.5
Ag	380	0.0	393		w			369	0.0
Au	405	0.0						394	0.0
B2g	537	0.0						512	0.0
B2u	547	0.5	528	530	w			516	0.1
B3g	580	0.0						552	0.0
B3u	587	28.9	555	560	s			565	20.2
B1u	647	1.6	640		w			631	1.2

Calculations were carried out by G03W using the B3LYP/6-311++G* method and basis set. ν is frequency (cm^{-1}) (s = solid, l = liq), and I is intensity (km/mole) from the G03 calculations or as relative strength, s = strong, m = medium, (v)w = (very) weak, for experimental measurements. For intermolecular mode assignments see Higgins et al. The lowest two frequencies reported in our experimental spectra of solid isomers are intermolecular modes.

3.3. 1,4-Dicyanobenzene

The lower panel of Fig. 3 shows the solid and solution FTIR, THz, and calculated spectra for the 1,4-DCB isomer. The high and low spectrally separated regions observed for the other two isomers also occurs for the 1,4-DCB isomer. There are four main absorption features

in the high frequency range of the solid-state spectrum. The chloroform solution spectrum agrees very well with the solid-state spectrum but with minor blue shifts. These blue shifts might again arise from the sharpening of the features in solution. Strong solvent absorptions mask the features at 363 cm^{-1} and 640 cm^{-1} observed for the solid phase spectrum.

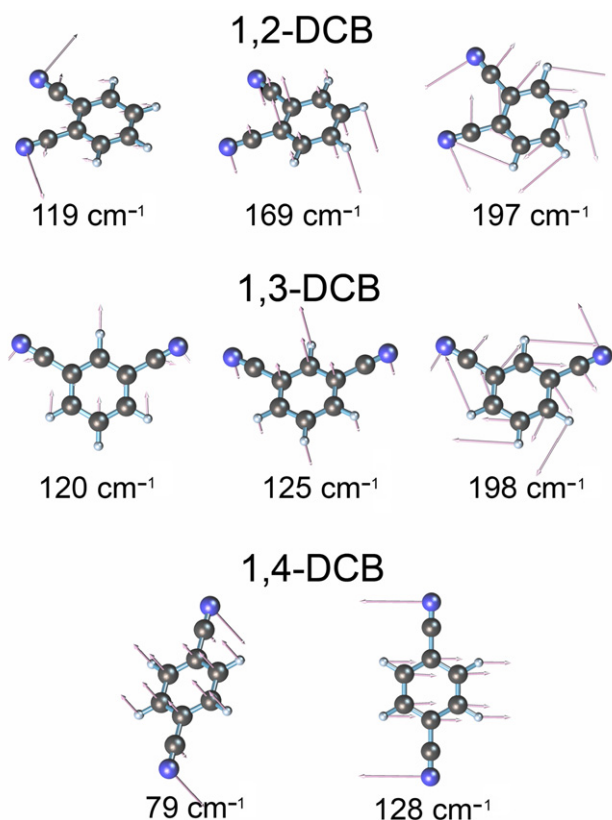


Fig. 4. Displacement vector representation of the lowest non-zero IR-active modes of the 1,2- 1,3- and 1,4-DCB isomers obtained from vibrational analysis of optimized isolated gas phase structures.

The low frequency range of the far-IR spectrum of solid 1,4-DCB exhibits two features at 100 cm⁻¹ and 154 cm⁻¹. The absorption strength of the lowest feature is noticeably stronger compared to the corresponding band observed in solution at 112 cm⁻¹. The THz-TDS spectrum yields one additional absorption feature at 28 cm⁻¹ and there may be another weaker band at approximately 11 cm⁻¹. Due to the limited bandwidth of the instrument, we could not fully resolve this lower frequency mode. All the internal modes are accounted for in the predicted IR spectrum and are very closely correlated with the experimental frequencies for all three isomers. In addition, the solution THz spectrum of the 1,4-DCB isomer shows no observable features in the low frequency range and thus these two modes are identified as intermolecular modes of crystalline 1,4-DCB.

The absorption strengths of the 1,4-DCB intermolecular modes are slightly smaller compared to those observed from 1,2-DCB isomers, possibly due to structural differences in the crystals. In addition to having no permanent molecular dipoles the symmetric 1,4-DCB isomers are arranged in the unit cell such that the C–N groups of neighboring molecules oppose each other. This might result in strong local interactions between molecules but not a long-range interaction throughout the molecules such as the dipolar arrangement for 1,2- and 1,3-DCB.

4. Comparison of the DCB isomers

The low frequency spectral regions (<250 cm⁻¹) of the three isomers exhibit very rich, strong internal and intermolecular mode absorption features and the integrated absorption strength of these features are *anomalously large*. The peak intensities are almost an order of magnitude larger than those found for most organic compounds. For example, the peak extinction coefficients of organic molecules (i.e., phenols, stilbene and azobenzene) are in the range of 1–4 M⁻¹ cm⁻¹ (or 0.1–2 km/mol). The observed low frequency IR absorption features of DCB are comparable in magnitude to the stronger mid-infrared absorption intensities and have a peak extinction coefficient of ~20–40 M⁻¹ cm⁻¹ (or ~10–15 km/mol). Unlike in the mid-IR spectral range where the modes predominantly involve localized pendant group motions of the molecule (i.e., C≡N, C–C stretches), these internal modes are global and involve motions of all the atoms, as shown in Fig. 4. The atomic partial charges and associated dipole derivatives for THz modes are small for most systems; in general, the lower frequency absorptions are expected to be weak in amplitude compared to higher frequency vibrational modes. A likely source of enhanced absorption in the DCB systems is due to the delocalization of electrons throughout the molecular structure. Thus one would expect an increase in net-dipole derivatives from the ortho and meta cyano groups when they are added to the pi-bonded benzene ring. To the best of our knowledge, the DCB isomers are the only known compounds examined to date with such strong THz absorption features below 250 cm⁻¹.

The comparison of simulated to experimental spectra helps assign and analyze the observed vibrational features and resulted in two significant observations. First, the internal modes observed in this low-frequency region do not induce strain on the benzene ring (Fig. 4). The ring itself does not stretch, expand or bend as is the case for ring deformation modes (>350 cm⁻¹). Second, the vibrational mode observed at 79 cm⁻¹ (from the calculation) of the 1,4-isomer is an out-of-plane mode which shifts ~45 cm⁻¹ to higher frequency for the 1,3-DCB isomer and ~90 cm⁻¹ for 1,2-DCB isomer. The solution and solid-state spectral features modes produced ~65 cm⁻¹ and ~77 cm⁻¹ blue shifts, respectively. The existence of such strong shifts for both gas phase calculations and solution spectra indicates that the shift is due to the internal rearrangement of the electronic charge distributions when the second cyano group is placed at the 4 versus the 2 position on the benzene ring. This not only breaks the internal symmetry but also brings the two CN groups closer to each other, increasing the intramolecular interactions. The other observed internal modes are in-plane modes and exhibit less than 10 cm⁻¹ lower frequency shift when the solution spectra of the isomers are compared (see Table 1).

A significant result when comparing the solid spectra of all three isomers to their solution and simulation spectra is

that the intensities of the out-of plane modes are significantly enhanced in the solid-state spectra. The enhancement is clearly observed, particularly for 1,2-DCB when the solution and simulation spectra are compared to the solid spectrum. The results suggest that this enhancement is a result of strong coupling of these out-of-plane modes with the strong crystalline phonon modes of this isomer.

Another sign of strong coupling of phonon-modes to out-of-plane internal modes is the appearance of a very weak feature at 181 cm^{-1} that is otherwise IR-inactive. The mode observed at 181 cm^{-1} of 1,3-DCB solid spectra has no counterpart both in solution and simulated spectra. Perhaps phonon-to-internal mode coupling might induce intensity to this originally IR-inactive state by deforming the symmetry of the motion. Solid-state calculations that reproduce the spectral features (both internal and intermolecular) would help confirm the origin of these observed strong interactions. We believe a complete theoretical study of these concepts would be a good exercise for solid-state theorists to better characterize such strong intermolecular couplings.

5. Conclusions

Terahertz vibrational spectra of 1,2-, 1,3-, and 1,4-dicyanobenzene isomers were collected by FTIR and THz-TDS for solid and solution phase samples and simulated with G03 using the B3LYP/6-311++G* level/basis combination. Two low frequency intermolecular modes were observed below $\sim 100\text{ cm}^{-1}$ and identified for all three isomers. Comparison of amplitudes observed in solid-state spectra to simulation and solution spectra suggest strong coupling of phonon modes with out-of-plane modes but not with in-plane modes. Spectral comparisons suggest that intermolecular interactions are considerably weak, (absent in solution) so the gas-phase simulation spectrum closely mimics that of the condensed-phase spectra. The 1,2-DCB isomer with the strongest static dipole moment and long-range dipolar arrangement of all the crystal structures showed the strongest absorption amplitudes for the lowest intermolecular modes.

This study yielded two significant observations: (1) The observed amplitudes of the lowest internal modes of DCB isomers are, to our knowledge, the strongest low frequency absorption features reported to date. The spectral results

produced almost an order of magnitude higher extinction coefficients for these isomers compared to similar organic molecules. (2) Reliable use of a cost-effective DFT software package for classification of the observed modes as intermolecular and intra-molecular modes and assignment of the low-frequency internal modes of weakly interacting organic systems is possible. These isomers and their readily identifiable spectral features may be of great interest in future studies utilizing THz spectroscopy to analyze internal and phonon mode properties of weakly interacting species in solids.

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