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Reassignment of the Vibrational Spectrum of Benzimidazole

J. Tomkinson*

Science and Technology Facilities Council, The ISIS Facility, The Rutherford Appleton Laboratory, Chilton OX11 0QX, U.K.

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New spectroscopic data on benzimidazole and benzimidazole-d_2, using inelastic neutron scattering spectroscopy, has revealed previously unobserved bands. These new observations are incorporated into a complete assignment of the benzimidazole spectrum and shown to agree well with ab initio calculations on the system. The new assignment scheme eigenvectors have been correlated to those of indole.

Introduction

Benzimidazole has some claim to technological importance (through its use in corrosion inhibition), biochemical importance (through its ability to bind metals, as in vitamin B_{12}), and pharmaceutical importance (in veterinary drugs). Our interest stems from its relationship to other heterocyclic systems and, as part of a broader study comparing the vibrational eigenvectors of 6−5 bicyclic heterocycles (like the nitrogenous heterocyclic bases of the nucleotides), we have made a brief study of benzimidazole's vibrational spectroscopy.

Benzimidazole has attracted some modest attention, in recent years, from groups attempting to assign optical data with the aid of ab initio calculations.[1–3] The optical data currently available is essentially the same as that from 40 years ago when the IR spectra of benzimidazole and benzimidazole-d_2 were first published.[4] However, there are complications; some optical features are not reported by all authors, and overtones are scattered across the range, especially above 1400 cm^{-1}. Clearly, given that 33 internal modes have to be assigned below 1700 cm^{-1}, there is room for confusion in the assignment of its spectrum, and indeed, only some half-dozen optical features in the solid are assigned consistently by all authors.

Given our interest in the molecular vibrational eigenvectors we have selected to use inelastic neutron scattering (INS) spectroscopy in this work. This is a well-understood vibrational technique that is matched to the study of hydrogenous molecular-crystalline systems.[5] The very much larger neutron scattering cross section of hydrogen emphasizes the vibrational modes involving these atoms. This, taken along with our ability to calculate, simply, the observed band intensities directly from the output of ab initio calculations, enables a more assured assignment procedure.

Here we report the INS spectra of benzimidazole and benzimidazole-d_2. We shall take advantage of the 20-fold difference in the neutron scattering cross sections of hydrogen and deuterium. INS transitions involving mostly deuterium displacements are very weak when compared with the equivalent hydrogenous modes. This will enable us to definitively assign some modes, and these assignments will disagree with all those previously published. We shall compare the observed spectra with that calculated from an ab initio approach. This will enable us to assign all the features of our INS spectra in accordance with the already published IR and Raman spectra. Finally we shall compare the form of the vibrations of benzimidazole with those of indole.

Crystallographic and Calculational Considerations

Benzimidazole crystallizes in the orthorhombic system, space group no. 33 ($Pna2_1$ or C^9_{2v}), and four molecules to the unit cell.[6] Each molecule is linked to its neighbors in adjacent cells by hydrogen bonds, where the $R(\text{NH}\cdots\text{N}')$ distance is 2.90 Å.[6] The local symmetry of the molecules is almost C_{2v}, and early studies of the system assumed this simplifying approach.[4]

Ab Initio Calculations. Our calculations were performed in GAUSSIAN98[7] for the isolated molecule of benzimidazole. In GAUSSIAN98 the molecular geometry was constrained planar and optimized at the B3LYP level; these density functional theory (DFT) calculations (with the 6-31G** basis set) produced harmonic vibrational frequencies. The atomic displacement vectors appearing in the output files were used as input to the ACLIMAX program, see below.

We also performed a naïve dimer calculation. Here two benzimidazole molecules, with geometry taken from the results of the isolated molecule calculation, were arranged alongside one another with a linear NH···N bond. The dihedral angle between the two molecules, at the NHN bond, was about 90°, an arrangement that was chosen for convenience but which is, crudely, representative of the arrangement of the molecules in the crystallographic lattice.

Data Visualization. ACLIMAX[8] is a stand alone program used to display the INS spectra and compare them with the results of ab initio calculations. Unlike optical spectroscopy, the INS technique readily expresses not only fundamentals but also all combination bands and overtones; fortunately these intensities are readily computed in ACLIMAX. Critical to the appearance of strong INS features (fundamentals, overtones, or combinations) is the reduced mass of the vibration involved. Generally, low reduced mass oscillators produce strong fundamentals and overtone sequences in INS and also show significant H/D isotope shifts in optical spectroscopy.[5]

Spectral Comparison. The calculated spectra of structurally related molecules can be profitably compared through the form of the atomic displacements of given modes, their eigenvectors. This can be attempted by inspection using commercial visualization packages. However, such comparisons are rather more subjective than is desirable and cannot be quantified. Fortunately, the comparison can be made quantitative by using the ViPA program.[9]

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* E-mail: j.tomkinson@rl.ac.uk.

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TABLE 1: Comparison of the Principal Structural Parameters of Benzimidazole, Measured and Calculated[a]

	experiment	calculation		
		B3LYP 6-311G(d,p)	B3LYP 6-31G*	this work dimer
	[6]	[3]	[2]	
		Lengths, angstroms		
a	1.346	1.304	1.378	1.372
b	1.311	1.377	1.307	1.313
c	1.395	1.389	1.391	1.389
d	1.389	1.398	1.400	1.402
e	1.386	1.388	1.390	1.392
f	1.401	1.407	1.410	1.412
g	1.378	1.390	1.392	1.394
h	1.401	1.394	1.396	1.399
i	1.372	1.384	1.385	1.386
j	1.392	1.415	1.416	1.419
r(N−H)	0.90	1.007	1.009	1.026
R(NH···N′)	2.90			3.018
		Angles, deg		
a, b	114.0	114.1	113.7	114.2
b, c	104.2	104.9	104.6	104.4
c, d	130.0	129.9		129.9
d, e	117.8	118.0	118.1	118.1
e, f	120.9	121.2	121.4	121.3
f, g	122.3	121.5	121.6	121.6
g, h	116.1	116.8	116.7	117.0
h, i	131.9	132.9		132.9
h, j	122.4	122.5	122.6	122.1
i, j	105.8	104.6	104.4	105.0
j, c	109.5	110.1	110.5	110.1
j, d	120.6	120.0	119.7	120.0
i, a	106.6	106.4	106.7	106.3

[a] Here, see Figure 1 for the atom numbering; the bond between atoms 1 and 2 is *a*; (2 and 3) *b*; (3 and 4) *c* and *d*; (4 and 5) *e*; (5 and 6) *f*; (6 and 7) *g*; (7 and 1) *h* and *i*; the last bond, *j*, lies between the unnumbered atoms. The bond angles are labelled, e.g., *a*, *b* indicates the $N_1-C_2-N_3$ angle.

Experimental Section

Samples. A sample of benzimidazole was obtained from the Aldrich Chemical Co. and used without further purification. The N_1-C_2 deuterated sample was produced by recrystallization of the perproto-benzimidazole from D_2O. Stirring strongly in a 1000-fold excess of D_2O, at 50 °C, it dissolved after 4 days giving a clear solution, which was evaporated to yield the benzimidazole-d_2. That deuteration occurs at the C_2 position has been demonstrated previously.[4] The isotopic purity of the compound was not determined.

Spectrometer. The samples were wrapped in aluminum foil (3.4 g of benzimidazole, 0.68 g of benzimidazole-d_2) and held in flat sample cells. These were maintained at 20 K in the neutron beam of the TOSCA spectrometer,[10] at the ISIS Facility, The Rutherford Appleton Laboratory, Chilton, OX11 0QX, U.K. TOSCA is a pulsed neutron, indirect geometry, low band-pass spectrometer with good spectral resolution ($\Delta E_t/E_t \approx 2\%$).[10] Data were collected for about 6 h and transformed into the conventional scattering law versus energy transfer (where E_t is given in cm^{-1}), using standard programs.

Calculated Structural Results. The GAUSSIAN98 calculated molecule of benzimidazole had a dipole of 3.5745 D, an energy of −379.893386 hartree, and rotational constants of 3924.62, 1671.82, and 1172.40 MHz. The principal structural parameters of benzimidazole are compared to those measured[6] and calculated by other workers[2,3] in Table 1.

Results and Assignments. The INS spectra of benzimidazole and benzimidazole-d_2 are shown in Figure 1 and detailed in Table 2. The lowest internal modes appear about 230 cm^{-1}, reasonably separated from the external modes that end at 177 cm^{-1}. Excellent agreement between the observed frequencies of the optical and the INS bands for both systems can be seen from the entries in Table 2. However, there are two exceptions to this generality: first, some strong INS bands, for which no optical counterpart has been reported; second, the many reported optical transitions for which there are no specific INS bands, mostly appearing above 1300 cm^{-1}. Above about 1200 cm^{-1} the strength of the vibrational transitions in the INS spectra of TOSCA falls away, and we loose our ability to make straightforward assignments. We shall, therefore, limit our INS assignments to transitions appearing below 1200 cm^{-1}, relying on the already published optical data[1-4,11,12] to complete the range.

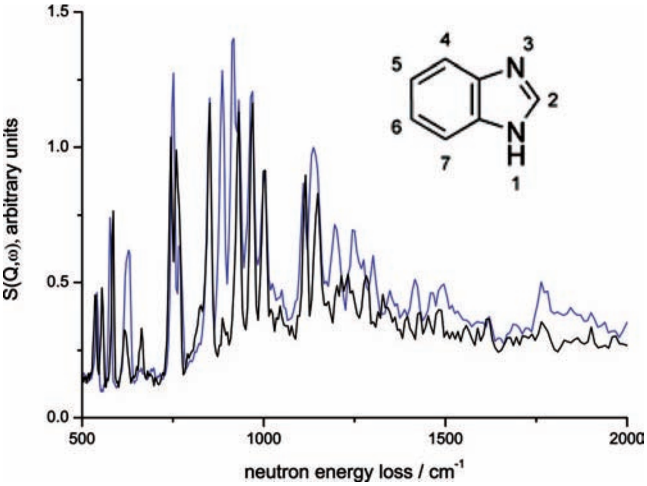

Figure 1. INS spectra of benzimidazole, blue trace, and benzimidazole-d_2, black trace, at 20 K. The molecular structure of benzimidazole, and its atom numbering scheme, is also shown.

Immediate Assignments. At 1777 cm^{-1} a significant INS transition is observed, see Figure 1. This is in the region of heavy atom stretches, like $\nu(C{=}O)$, but this band must arise from a hydrogen displacement to have any significant INS intensity, which immediately implies its assignment as an overtone.[5] This overtone could only, reasonably, arise from a low reduced mass, purely harmonic, oscillator fundamental at 888 cm^{-1} (or from an anharmonic system of somewhat higher frequency). The two fundamentals observed at 886 and 918 cm^{-1} are possible candidates as origins of the overtone and both transitions, and the overtone, are totally absent from the INS spectrum of benzimidazole-d_2. The origin of the overtone in benzimidazole is, therefore, in the out-of-plane spectral mode region of the imidazole moiety and must be the $\gamma(CH)_{im}$ and $\gamma(NH)$. This is consistent with the fact that no intense overtones are found in this region of the INS spectrum of benzene.[13] Furthermore, the benzimidazole band at 852 cm^{-1} remains in the benzimidazole-d_2 INS, at 850 cm^{-1}, in contradistinction to the IR data. The impact of deuteration on this band, which appears so clear-cut from the IR, is less so from the INS data.

The assignment of the band at 918 cm^{-1} to $\gamma(NH)$ is readily acceptable. This out-of-plane mode is known to be a light mass oscillator in imidazole,[14] nicely satisfying the requirement for the observation of an overtone. It is also in harmony with $\gamma(NH)$ assignments in solid imidazole, optically at 958 cm^{-1} [15] and INS at 961 cm^{-1} ,[14] and agrees reasonably with the observation of $\gamma(NH)$ at 888 and 900 cm^{-1} in purine.[16]

In the isolated molecule $\gamma(NH)$ is calculated about 440 cm^{-1}, in line with other reports,[3,17] and it is assigned in this region in matrix isolation experiments, 459 or 449 cm^{-1}.[1,17] However, in

TABLE 2: Comparison of the Observed and Calculated Band Positions, cm^{-1}, of Solid Benzimidazole (H) and Benzimidazole-d_2 (D), below 2000 cm^{-1}[a]

optical results			calculated results					
IR[b]	Raman[b]	IR[b]	mono[c]	mono[d]	dimer[d]		INS results[d]	
H	H	D	H	H	H	D	H	D
228		221	223	**223**	**229**	213	231	223
242	246	237					244	236
274	269	271	255	**255**	**257**	250	271	
		406						
419		413	418	418	429	403	422	406
424	422	422	431	**430**	**432**	428		418
			438	**440**		339		
544	547	538	551	551	553	547	541	534
		557						555
578	581	584	587	**587**	**584**	595	581	583
619	620	614	628	628	628	626	624	620
628	628	627	647	**647**	**628**	550	632	
634	637	638						
								661
740	748	740	751	**751**	**751**	752	753	745
								759
760	752	750	766	**768**	**769**	768	772	767
		756						
769		764						
772		769						
778	780		790*	790	793	777	840	
837								
848	851		853	**853**	**852**	859, 726	852	
								850
880	884	887	865	**864**	**869**		886	
890	892		889	888	889	863		
					823	591	918	
897		920						
929	936	942	944	**943**	**937**	938	933	929
960	962		944	943	943	940		
		996	981	**981**	**976**	981	971	967
1006	1008	1004	1030	1030	1029	1029	1005	1001
1115	1112	1112	1132	1132	1131	1136	1111	1114
	1125							
1138	1139		1100	1101	1153	940	1132	
1155	1160	1159	1173	1173	1171	1170	1149	1144
1185	1191	1186	1206	1206	1215	1036	1190	
1200	1206	1221						
1250	1251	1240	1277	1277	1296	1244	1252	1240
		1253						
		1264						
		1276						
1263	1277	1283	1291	1290	1291	1269	1275	
1295	1306	1303	1341	1341	1339	1303	1307	
		1326						
1340								
1350	1349	1341	1388	1387	1398	1345	1350	
1360	1365	1366						
1380								
1410	1414	1411	1427	1427	1465	1402		
	1421	1430						
1435		1454						
1460	1463	1478						
1485	1481	1484	1484	1483	1493	1472		
1510	1500	1502	1526	1526	1525	1521		
1589	1592	1590	1541	1540	1553	1507		
			1629	1629	1629	1625		
1620	1623	1608	1668	1668	1671	1663		
							1777	

[a] Optical frequencies shown are the consolidated set from several authors (refs 1– 4, 11, and 12); those in bold are out-of-plane, and those in italic are in-plane modes (ref 12). Optical features with significant deuteration effects are underlined (ref 4). In the column reporting calculations on the deuterated monomer the band positions appear nonsequentially, in the order corresponding to their proton equivalent. The entry marked * mistakenly appears twice in this reference (ref 17). The calculated results refer to the cases of an isolated molecule, mono, or an isolated dimer, dimer. [b] Refs 1– 4, 11, and 12. [c] Ref 17. [d] This work.

its lattice the molecule is known to be hydrogen bonded to its neighbors.[6] Our naïve dimer calculation, see above, shows that the hydrogen bonding has a significant effect on the frequency of the γ(NH), moving it up to about 859 cm^{-1} and demonstrating that our assignment at 918 cm^{-1} is reasonable. The assignment is also given support by the mechanical anharmonicity (a well-established aspect of hydrogen bonds) needed to generate the overtone at 1777 cm^{-1}, which is some 60 cm^{-1} less than the harmonic value, 1836 cm^{-1} (= 2 × 918).

Moreover, this assignment allows for an explanation of its absence from the optical spectrum. This transition is calculated with sufficient IR intensity to have been observed; however, if it was accidentally degenerate with the 886 and 888 cm^{-1} bands it could have easily been missed in the room-temperature IR spectrum. Our INS data was obtained at 20 K, and intermolecular hydrogen bond out-of-plane modes are known to be temperature-sensitive, often moving some 20−40 cm^{-1} higher as the temperature falls.[18]

The assignment of $\gamma(\mathrm{CH})_{\mathrm{im}}$ is less straightforward because it is not localized on the imidazole moiety; rather the imidazole coordinate, $\gamma(\mathrm{CH})_{\mathrm{im}}$, is mixed with a benzenoid mode, $\gamma(\mathrm{CH})_{\mathrm{ben}}$. The bands observed at 886 cm^{-1} in benzimidazole and 850 cm^{-1} in benzimidazole-d_2 are clearly related to $\gamma(\mathrm{CH})_{\mathrm{im}}$, but the relationship is nontrivial, see below.

The optical transition observed at 1138 cm^{-1}, present in the INS of benzimidazole at 1132 cm^{-1}, was shown to be deuterium-sensitive[4] and is indeed absent from our benzimidazole-d_2 INS spectrum. It appears in the in-plane deformation region of the spectrum. The form of this vibration is discussed below. There is no evidence from our spectra of any other significant effects of deuteration above 1200 cm^{-1}. However, TOSCA spectra tend to lose sensitivity above this energy transfer value and there is an optical report of a deuterium-sensitive band at 1588 cm^{-1}.[4]

The optical band at 960 cm^{-1} was reported to be deuterium-sensitive[4] but is not specifically identified in any of our INS spectra (see below); therefore, it can have only a very modest involvement from hydrogen displacements and little deuterium shift. Its disappearance from the IR spectrum of benzimidazole-d_2 is not easily explicable, but a shift of only 1.02 would bring it accidentally degenerate with a deuterium-insensitive, out-of-plane, benzenoid mode. Interestingly, these modes are calculated to be accidentally degenerate in the isolated molecule, at 943 cm^{-1}.

Remaining Assignments. Having assigned several prominent vibrations directly from the INS spectra we are now in a position to compare the calculated INS spectrum with that observed. Preparative to this, we must identify the eigenvectors of the assigned modes in the GAUSSIAN98 calculations.[7] The γ(NH) eigenvector is immediately identifiable since it involves, almost exclusively, the displacement of this hydrogen atom.

Unlike γ(NH), the $\gamma(\mathrm{CH})_{\mathrm{im}}$ displacement never appears as a pure vibration. Rather, it is mixed with a benzenoid mode that appears at a similar frequency, $\gamma(\mathrm{CH})_{\mathrm{ben}}$. Due to the pseudo-$C_{2v}$ symmetry of benzimidazole the vibrations of the benzenoid moiety are not simply those of isolated benzene (for the form of benzene modes see ref 19). The $\gamma(\mathrm{CH})_{\mathrm{ben}}$ mode is composed (50:50) of the benzene modes ν_8 and ν_{11}. In turn this $\gamma(\mathrm{CH})_{\mathrm{ben}}$ mixes with $\gamma(\mathrm{CH})_{\mathrm{im}}$ to generate in- and out-of-phase components; these are calculated at ($\gamma(\mathrm{CH})_{\mathrm{ben}} + \gamma(\mathrm{CH})_{\mathrm{im}}$) 853 and ($\gamma(\mathrm{CH})_{\mathrm{ben}} - \gamma(\mathrm{CH})_{\mathrm{im}}$) 864 cm^{-1}, respectively, see Table 2. Upon deuteration the $\gamma(\mathrm{CD})_{\mathrm{im}}$ frequency falls, leaving the $\gamma(\mathrm{CH})_{\mathrm{ben}}$ standing alone, and the splitting collapses. In the INS spectra of benzimidazole, about half of the intensity in either the 853 or 864 cm^{-1} bands arises from the benzenoid component, and in benzimidazole-d_2 it accounts for all of the intensity in the remaining band, calculated at 850 cm^{-1}. In the IR most of the intensity comes from the imidazole contribution, which strength-

TABLE 3: Correlation of the GAUSSIAN98 Calculated Vibrations of an Isolated Benzimidazole Molecule with Those of Indole (Ref 20) below 1100 cm^{-1}; the Assigned Band Positions Are Also Given, "obsd"[a]

	A″						A′				
	indole		benzimidazole				indole		benzimidazole		
ν	obsd	G98	G98	obsd	%	ν	obsd	G98	G98	obsd	description[b]
42	239	222	223	240	99						ring−ring antiwag (butterfly)
41	265	256	255	271	94						ring−ring antitwist
					94	29	397	410	418	422	ring−ring antirock
40	429	445	430	422	97						Bz[91(20)]:Py[24(23), 14(19), 11(22)]
39	516	543	440	918	93						γ-NH
						28	542	562	551	541	Bz[52(18)]:Py[16(7), 11(18)]
38	578	597	587	580	97						Bz[43(20), 26(8)]:Py[26(23), 12(12)]
37	608	625	647	632	93						Bz[28(4), 15(11)]:Py[40(23), 29(12), 14(11)]
						27	619	630	628	624	Bz[55(18)]:Py[23(20), 10(9)]
36	730	748									Bz[−]:Py[50(22), 19(11), 14(12)]
35	758	777	751	753	81						Bz[36(4), 40(11)]:Py[21(11)]
					98	26	758	781	790	840	Bz[40(18), 26(6)]:Py[20(6), 14(19), 12(9)]
34		819	768	772	63						Bz[45(11), 40(8)]:Py[15(12), 14(21))]
33	854	888	865	889	81						Bz[36(11), 18(19)]:Py[55(21)]
					91	25	867	903	888		Bz[44(7), 10(18)]:Py[25(8), 17(9)]
32		911	853	852	51						Bz[24(19), 12(11)]:Py[64(10), 10(21)]
					81	24	896	925	943		Bz[18(14), 9(6)]:Py[40(9), 32(20)]
31	937	972	943	933	98						Bz[88(19)]:Py[−]
30	971	1020	981	971	98						Bz[67(2), 30(19)]:Py[6(10)]
					99	23	1006	1043	1030	1005	Bz[57(14), 31(6)]:Py[7(7)]

[a] The mode numbers, ν, refer to indole, and values in the "%" column represent the degree to which the eigenvectors of the two molecules correlate. [b] Description of the indole vibrations in terms of those of benzene and pyrole (ref 20).

ens the observed bands at 848 and 880 cm^{-1}, but this is lost on deuteration, and the band becomes insignificant.

Similarly the in-plane deformation mode, at 1132 cm^{-1}, calculated at 1153 cm^{-1} in the dimer, involves both in-plane deformations, δ(NH) and δ(CH)$_{\mathrm{im}}$. When the two coordinates vibrate in antiphase no other atomic displacements are involved, and the mode is totally absent from the calculated spectrum of benzimidazole-d_2. Unfortunately, when the coordinates vibrate in-phase they must involve contributions from the benzenoid moiety, and there will be but slight contrast between the benzimidazole and benzimidazole-d_2 INS spectra for this mode.

The displacement vectors for these modes, as input to ACLIMAX (see above[8]), have their calculated frequency values individually scaled to agree with the observed values, 852, 886, 918, and 1132 cm^{-1}, respectively.

The INS spectrum produced by ACLIMAX from the scaled ab initio output discussed above is compared to the observed spectrum in Figure 2, and it is now a relatively straightforward task to achieve a full assignment by inspection. Starting at the lowest frequencies, the calculated bands have their frequencies scaled to those of nearby observed spectral features of the same intensity. In doing this, we always ensure that we match the calculated and the optically determined characters of the modes.[12] Working up from lower frequencies avoids any confusion that might arise from overtone intensities appearing among the higher frequency modes. This process is straightforward across the spectrum, except that we are unable to give any assigned INS band positions to the modes calculated at 888, 943, and 1132 cm^{-1}. These modes sit close to strong INS features and contribute too little intensity to significantly modify the observed spectral profile. In our results they are assigned to features appearing in the optical spectra but are hidden by other bands in the INS. The final assignment is given in Table 2 and shown in Figure 3. The final spectrum was obtained with a typical value for the argument to the Debye−Waller factor, 0.02 Å^2 (as used in ACLIMAX[8]).

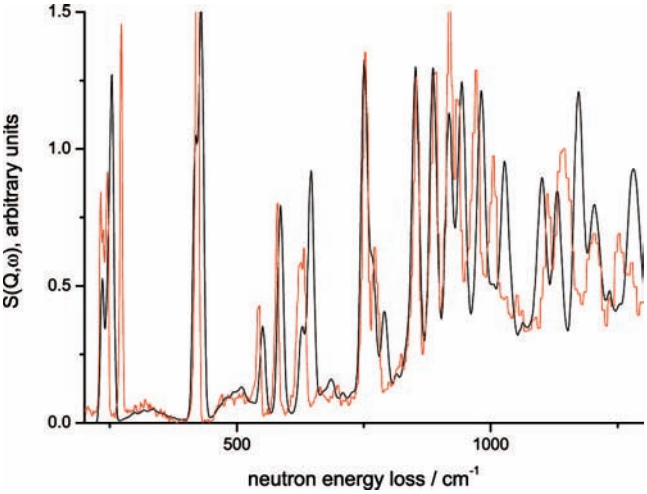

Figure 2. INS spectrum of benzimidazole, red trace, compared to the calculated spectrum, black trace, after the initial assignments made in the text.

Discussion

The assignment of γ(NH) at 918 cm^{-1} in the solid is in complete disagreement with the optical spectroscopic assignments that place it about 628 cm^{-1}.[2,4,11,12] The previous optical assignments were made on the basis that the greatest deuteration shift should be demonstrated by γ(NH), and in the absence of the 918 cm^{-1} band, the greatest shift was given by the 628 cm^{-1} feature. This value was also consistent with the assignment of γ(NH) in indole, 512 cm^{-1}.[20] In indole, however, the strength of the hydrogen bonding is weak because the H-bond acceptor is the benzenoid ring of a neighboring molecule; in benzimidazole a much stronger NH$\cdots$N bond is formed. Recent optical studies[1−3] dismissed the earlier optical results on crystalline imidazole, where γ(NH) is assigned at 958 cm^{-1},[15] and ignored its INS study, where γ(NH) is assigned at 961 cm^{-1}.[14]

In our spectra the benzimidazole band, observed at 628 cm^{-1} in the IR, appears at 632 $^{-1}$ and shifts to 555 cm^{-1} on deuteration

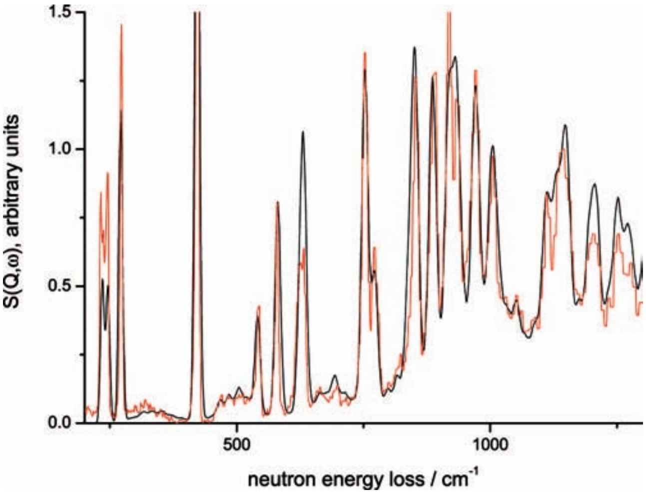

Figure 3. INS spectrum of benzimidazole, red trace, compared to the calculated spectrum, black trace, of the final assignment.

(agreeing with optical data), but significantly, it retains INS intensity. The vibrational mode, thus, involves displacements of the benzenoid hydrogen atoms. The vibrational displacements of this mode correlate very well (better than 90%, see below) with those of indole in the same mode (observed at 608 cm^{-1} [20]). This vibration, in indole, is a 40:60 mixture of benzene and pyrole modes and involves, principally, out-of-plane displacements of the C and N atoms, entraining their attached hydrogen atoms. In our INS spectrum the 632 cm^{-1} band is rather too weak in comparison to that calculated. This is probably linked to the weakness of the calculated band at 223 cm^{-1}, observed as a doublet at 231 and 244 cm^{-1}. (The calculated spectrum of the hydrogen-bonded molecule in the dimer gives a distribution of intensities that are much closer to those observed.) Here we briefly note two very weak, but visible, features of the INS spectrum, at 696 and 1055 cm^{-1}; they are both accurately accounted for by ACLIMAX and are combinations involving the 420 cm^{-1} band and strong features at 270 and 632 cm^{-1}.

We have correlated the calculated vibrational displacements of benzimidazole with those of indole using the ViPA program.[9] This is a quantitative comparison of the eigenvectors of the two molecules, and we expect a high degree of correlation between these molecules of very similar geometry. The results of this exercise is given in Table 3 (the table also shows a description of the indole modes in terms of those of their basis molecules, benzene and pyrole[20]). As in the case of indole, several benzimidazole modes are seen to be localized on either the benzene or the imidazole rings. As anticipated there is an excellent degree of correlation, generally better than 90%, all better than 80%, except for the modest correlation to the indole modes ν_{32} (51%), ν_{34} (63%), and ν_{36}. These are all out-of-plane modes, and the disparity arises from the mass differences between carbon and nitrogen except for ν_{36}; here there can be no correlation since this is the γ(CH) of the extra hydrogen atom in indole.

Conclusion

New spectroscopic data on benzimidazole and benzimidazole-d_2, using INS spectroscopy, has revealed two previously unobserved bands. These new bands are out-of-plane modes. The complete INS spectrum, to 1200 cm^{-1}, was assigned in good agreement with ab initio calculations, and the eigenvectors were correlated to those of indole.

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References and Notes

(1) Klots, T. D.; Devlin, P.; Collier, W. B. *Spectrochim. Acta* **1997**, *53A*, 2445–2456.

(2) Morsy, M. A.; Al-Khaldi, M. A.; Suwaiyan, A. *J. Phys. Chem. A* **2002**, *106*, 9196–9203.

(3) (a) Sundaraganesan, N.; Ilakiamani, S.; Subramani, P.; Dominic Joshua, B. *Spectrochim. Acta* **2007**, *67A*, 628−635. (b) Mohan, S.; Sundaraganesan, N.; Mink, J. *Spectrochim. Acta* **1991**, *47A*, 1111−1115.

(4) Cordes, M. M.; Walter, J. L. *Spectrochim. Acta* **1968**, *24A*, 1421–1435.

(5) Mitchell, P. C. H., Parker, S. F., Ramirez-Cuesta, A. J.; Tomkinson, J. *Vibrational Spectroscopy with Neutrons*; World Scientific Press: Singapore, 2005.

(6) Dik-Edixhoven, C. J.; Schent, H.; Van der Meer, H. *Cryst. Struct. Commun.* **1973**, *2*, 23–25; see also the Cambridge Crystallographic Database 2001 refcode BZDMAZ02.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M. E.; Replogle S.; Pople, J. A. *GAUSSIAN98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Ramirez-Cuesta, A. J. *Comput. Phys. Commun.* **2004**, *157*, 226–238.

(9) Grafton, A. K.; Wheeler, R. A. *Comput. Phys. Commun.* **1998**, *113*, 78–84.

(10) Colognesi, D.; Celli, M.; Cilloco, F.; Newport, R. J.; Parker, S. F.; Rossi-Albertini, V.; Sacchetti, F.; Tomkinson, J.; Zoppi, M. *Appl. Phys. A* **2002**, *74* (Suppl), S64–S66; also: http://www.isis.rl.ac.uk/molecularSpectroscopy/tosca/index.htm.

(11) Borah, B.; Wood, J. L. *Can. J. Chem.* **1976**, *54*, 2470–2481.

(12) Suwaiyan, A.; Zwarich, R.; Baig, N. *J. Raman Spectrosc.* **1990**, *21*, 243–249.

(13) Kearley, G. J.; Johnson, M. R.; Tomkinson, J. *J. Chem. Phys.* **2006**, *124*, 044514.

(14) Loeffen, P. W.; Pettifer, R. F.; Fillaux, F.; Kearley, G. J. *J. Chem. Phys.* **1995**, *103*, 8444–8455.

(15) Perchard, C.; Bellocq, A.; Novak, A.; Josien, M. L. *J. Chim. Phys. (France)* **1965**, *62*, 1344.

(16) Parker, S. F.; Jeans, R.; Devonshire, R. *Vib. Spectrosc.* **2004**, *35*, 173–177.

(17) Schoone, K.; Smets, J.; Houben, L.; VanBael, M. K.; Adamowicz, L.; Maes, G. *J. Phys. Chem. A* **1998**, *102*, 4863–4877.

(18) Novak, A. *Croat. Chem. Acta* **1982**, *55*, 147–169.

(19) Herzberg, G. *Molecular Spectra and Structure, II Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1945; p 118.

(20) Tomkinson, J.; Riesz, J.; Meredith, P.; Parker, S. F. *Chem. Phys.* **2008**, *345*, 230–238.

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