

# Vibrational analysis of the imidazolate ring

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Abstract—IR and Raman spectra have been investigated for imidazolate and 4-methylimidazolate including five and three deuterated analogs, respectively. Assignment of the observed IR and Raman bands has been made on the basis of isotopic frequency shifts, Raman polarization properties, and normal coordinate calculations. The calculated normal frequencies are in good agreement with experimental ones; the average error below 1600 cm<sup>-1</sup> is 4.5 cm<sup>-1</sup> for 104 in-plane vibrations and 3.8 cm<sup>-1</sup> for 43 out-of-plane vibrations. The calculated vibrational modes are useful in analyzing the Raman bands of histidine residues in proteins.

### INTRODUCTION

THE IMIDAZOLE ring of histidine carries two nitrogens, which can be protonated or deprotonated individually. The protonated nitrogen usually acts as a proton donor in hydrogen bonding, while the deprotonated nitrogen accepts a hydrogen atom from proton donors or ligates to a metal cation. In proteins, the imidazole ring of histidine takes one of three forms: fully protonated and cationic (imidazolium, ImH<sub>2</sub><sup>+</sup>), partially protonated and neutral (imidazole, ImH), and fully deprotonated and anionic (imidazolate, Im<sup>-</sup>). These three forms are inter-convertible in proteins and such versatility of histidine is utilized in structural organization of proteins and in proton translocation in enzymatic reactions.

Raman spectroscopy is one of the useful techniques for studying the structures of proteins. Aromatic amino acid residues such as tryptophan and tyrosine give strong Raman bands with both visible and UV excitations, and much structural information can be obtained from the spectra. For histidine residues, however, structural information obtainable from Raman spectra is rather limited, mainly because Raman scattering from histidine is weak compared to that from other aromatic residues. As an exception, the imidazolium ring with both nitrogens deuterated  $(ImD_2^+)$  gives a strong Raman band with visible excitation, which is characteristic of its cationic form and can be used to study the  $ImD_2^+ \leftrightarrow ImD$  equilibrium in proteins [1-5]. The relative weakness of Raman scattering does not alter even with UV excitation for ImH<sup>+</sup> and ImH [6]. On the other hand, the UV absorption of  $Im^-$  is red-shifted with respect to that of  $ImH_2^+$  and  $ImH_2^-$ [7, 8], and a significant resonance enhancement of Raman scattering is expected for Im<sup>-</sup> if an appropriate excitation wavelength is employed. Recently we have demonstrated that the Raman scattering from the Im<sup>-</sup> ring that bridges two metal cations in Cu,Zn-superoxide dismutase can be readily detected with 240 nm excitation [8]. In order to exploit the Im<sup>-</sup> Raman bands in protein structural studies, it is required to establish the normal modes of Im<sup>-</sup> vibrations. Although several studies have been made on vibrational analysis of ImH and ImH<sub>2</sub><sup>+</sup> [9-14], there is no report on systematic analysis of the normal vibrations of Im<sup>-</sup> to our knowledge.

In this study, we have measured infrared (IR) and Raman spectra of six isotopomers of Im<sup>-</sup>  $(d_0, 2 \cdot d_1, 5 \cdot d_1, 2, 5 \cdot d_2, 4, 5 \cdot d_2, and 2, 4, 5 \cdot d_3)$  and four isotopomers of 4-methylimidazolate (4-MeIm<sup>-</sup>;  $d_0, 2 \cdot d_1, 5 \cdot d_1, and 2, 5 \cdot d_2)$  in alkaline aqueous solution. The observed IR and Raman bands have been assigned on the basis of isotopic frequency shifts and Raman polarization properties. We have made normal coordinate calculations to obtain a set of force constants, which reproduce experimental data satisfactorily and confirm the experimental assignments.

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#### EXPERIMENTAL

ImH was purchased from Nacalai Tesque and purified by recrystallization from water. 4-Methylimidazole (4-MeImH) was obtained from Tokyo Kasei Chemicals and purified according to the literature method with slight modifications [15]. Deuteration at ring carbons of ImH and 4-MeImH was performed by using hydrogen-deuterium exchange reactions at high temperatures [16]. Briefly, ImD-2- $d_1$  was prepared by heating ImH in D<sub>2</sub>O at 50°C (pD 8.0) for 2 days. The fully deuterated imidazole, ImD-2,4,5- $d_3$ , was obtained by heating a D<sub>2</sub>O solution of ImH at 250°C for 4 days in a high pressure reaction vessel. H-D exchange for a shorter period (1.5 days) at 250°C gave a mixture of ImD-2- $d_1$ , -2,5- $d_2$ , and -2,4,5- $d_3$ . The D $\rightarrow$ H back reaction at position 2 was made at 50°C in H<sub>2</sub>O to obtain ImH-4,5- $d_2$  from ImD-2,4,5- $d_3$ . Deuteration of 4-MeImH was performed in the same way as described for ImH to obtain 4-MeImD-2- $d_1$ , -5- $d_1$ , and -2,5- $d_2$ . The deuterated compounds. <sup>1</sup>H-NMR spectra in D<sub>2</sub>O showed that the isotopic purity was better than 95% for ImD-2- $d_1$ , 4-MeImD-2- $d_1$ , -5- $d_1$ , and -2,5- $d_2$ , and it was better than 80% for the other deuterated isotopomers.

ImH, 4-MeImH, and their deuterated analogs were converted into the Im<sup>-</sup> form by dissolving the compounds in KOH-saturated  $H_2O$  at a concentration of 7 M, and IR absorption spectra were recorded on a Jasco FT/IR-7000 spectrometer by holding the solution between two ZnSe plates without a spacer. The broad absorption band due to solvent H<sub>2</sub>O was subtracted from the solution spectra. For Raman measurements, the imidazolates were prepared in 3 M KOH aqueous solution at a concentration of 0.1 M. Raman spectra were excited with 488.0 nm radiation from an Ar ion laser and recorded on a Jasco CT-80D double monochromator equipped with an intensified diode array detector (Princeton Instruments, D/SIDA-700I/G) or on a Jasco RC 60P single monochromator equipped with a prism filter and a liquid nitrogen-cooled CCD (Princeton Instruments, LN/CCD 1152). Wavenumbers of Raman bands were calibrated with the spectrum of indene. Bands due to isotopic impurities were subtracted from the raw IR and Raman spectra. Such spectral subtraction was particularly helpful in obtaining the IR and Raman spectra of Im<sup>-</sup>-2,4-d<sub>2</sub> because the isotopomer was prepared only as a mixture with  $Im^{-}-2-d_{2}$  and  $-2,4,5-d_{3}$ . The IR and Raman spectra to be reported here are those obtained for pure isotopomers by spectral subtraction. Peak frequencies of IR and Raman bands are generally coincident with each other within experimental error  $(\pm 1 \text{ cm}^{-1})$ . Exceptionally, however, IR and Raman frequencies of a few vibrations differed from each other by 5 cm<sup>-1</sup> at most, possibly due to different sample concentrations. In such a case, we chose the frequency of either the IR or Raman band according to which appeared more clearly.

## NORMAL COORDINATE CALCULATIONS

Calculations of normal vibrations and the least-squared refinements of force constants were made by use of the computer program NCTB [17] based on the *GF* matrix method. Figure 1 shows the atom numbering scheme for  $Im^-$ . The geometrical parameters used in the calculations are listed in Table 1. The skeletal ring geometry was taken from the X-ray crystal data on  $Cu^{2+}-Im^--Cu^{2+}$  [18] and small modifications of the parameters were made to attain  $C_{2v}$  symmetry. The ring C-H bond was assumed to be 1.087 Å in



Fig. 1. Atom numbering scheme for the imidazolate ring.

Table 1. Geometrical parameters of the imidazolate ring used in the normal coordinate calculations

Bond length	(Å)	Bond angle (°)		
$N_1 - C_2, C_2 - N_3$	1.331	N <sub>1</sub> C <sub>2</sub> N <sub>3</sub>	113.6	
$N_{7}-C_{4}, N_{1}-C_{5}$	1.374	$C_2N_3C_4$ , $C_2N_1C_5$	104.5	
C <sub>4</sub> -C <sub>5</sub>	1.350	$N_3C_4C_5$ , $N_1C_5C_4$	108.7	
C-H	1.087	$N_1C_2H$ , $N_3C_2H$	123.2	
C <sub>c</sub> -CH <sub>3</sub>	1.517	$N_3C_4H$ , $C_5C_4H$	125.7	
, ,		$N_1C_5H$ , $C_4C_5H$	125.7	

length and to bisect the CCN or NCN angle. For 4-MeIm<sup>-</sup>, the C-CH<sub>3</sub> length was assumed to be the same as that of *p*-cresol [19]. The methyl group was treated as a point mass of 15 amu because the methyl vibrations were easily identified in the spectra and no strong vibrational coupling was expected between the methyl group and the imidazolate ring.

Internal coordinates were defined following the IUPAC recommendation [19, 20]. The coordinates of Im<sup>-</sup> consist of eight stretches ( $\nu$ CC, 4  $\nu$ CN, and 3  $\nu$ CH) and eleven bends (2  $\phi$ CCN, 2  $\phi$ CNC,  $\phi$ NCN, 2  $\phi$ CCH, and 4  $\phi$ NCH) for in-plane vibrations, and three waggings (3  $\pi$ CH) and five torsions ( $\tau$ CC and 4  $\nu$ CN) for out-of-plane vibrations. In the case of 4-MeIm<sup>-</sup>, the coordinates involving the C<sub>4</sub>-H bond of Im<sup>-</sup> were replaced by those involving the C<sub>4</sub>-CH<sub>3</sub> bond. A general valence force field was employed and the force constants were expressed in terms of these internal coordinates.

In calculating the G and F matrices, the following linear combinations were chosen to remove redundancy coordinates:

$$\delta C_j H = (\phi X_i C_j H - \phi X_k C_j H)/2^{1/2}$$
  
$$\gamma X_i C_j X_k = (2\phi X_i C_j X_k - \phi X_i C_j H - \phi X_k C_j H)/6^{1/2}$$

Here X is C or N, and the subscripts denote atom indices. Similar linear combinations were also employed for bending coordinates at  $C_4CH_3$  of 4-MeIm<sup>-</sup>. The other redundancies, arising from ring constraints, were not eliminated explicitly and 6 zero-frequency modes corresponding to the redundancies were obtained in the process of *GF* matrix diagonalization.

Initial values of force constants were taken from the results of *ab initio* calculations on ImH [11] and general valence force fields for *p*-cresol [19] and pyrrole [21]. Refinements of the force constants were made by least squares fitting of the calculated frequencies to the experimental ones. Normal coordinate calculations were first made for Im<sup>-</sup> and its deuterated isotopomers. Then the force field obtained was further refined by extending the calculations to 4-MeIm<sup>-</sup> and its deuterated isotopomers.

#### **RESULTS AND DISCUSSION**

The normal vibrations of Im<sup>-</sup> are classified into  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  species under  $C_{2\nu}$  symmetry, the  $A_1$  and  $B_1$  modes being in-plane and the  $A_2$  and  $B_2$  modes out-of-plane. All the modes are Raman active and all but the  $A_2$  modes are IR active. Raman bands due to the  $A_1$  modes are polarized while those due to the other modes are depolarized. Figure 2 shows IR and Raman spectra of Im<sup>-</sup> and its deuterated isotopomers in the 1600-500 cm<sup>-1</sup> region.  $5A_1$ ,  $5B_1$ ,  $2A_2$  and  $3B_2$  modes are expected in the frequency region shown, in addition to three C-H (C-D) stretching vibrations ( $2A_1$  and  $1B_1$ ) having much higher frequencies. Assignment of the observed IR and Raman bands is rather straightforward for Im<sup>-</sup>- $d_0$  and symmetrically deuterated isotopomers, Im<sup>-</sup>-2- $d_1$ , -4,5- $d_2$ , and -2,4,5- $d_3$ . We will briefly describe how we have assigned the IR and Raman bands of Im<sup>-</sup>- $d_0$  shown in Fig. 2A. Below 1600 cm<sup>-1</sup>, we found five polarized Raman bands at 1456, 1249, 1142, 1099, and 945 cm<sup>-1</sup>. These Raman bands and the corresponding IR bands are unequivocally assigned to the  $A_1$  modes. Since the out-of-plane



Fig. 2. IR (upper) and Raman (lower) spectra of  $Im^--d_0$  (A),  $Im^--2-d_1$  (B),  $Im^--4,5-d_2$  (C),  $Im^--2,4,5-d_3$  (D).



Fig. 2.  $\text{Im}^{-5-d_1}(\text{E})$ ,  $\text{Im}^{-2.5-d_2}(\text{F})$ . Bands marked with + are due to impurities in the ZnSe plates.

vibrations are expected below 900 cm<sup>-1</sup>, five IR bands at 1459, 1306, 1225, 1080, and 927 cm<sup>-1</sup>, most of which are accompanied by weak and depolarized Raman bands, are assigned to the  $B_1$  in-plane modes. Below 900 cm<sup>-1</sup>, three IR bands at 846, 783, and 689 cm<sup>-1</sup> are ascribed exclusively to the  $B_2$  out-of-plane modes because the  $A_2$  out-of-plane modes are IR inactive. The Raman band at 658 cm<sup>-1</sup>, which does not have a counterpart in the IR spectrum, is assigned to an  $A_2$  mode. The other  $A_2$  mode is not apparent in the Raman spectrum. Since the  $A_2$  vibrations do not involve any motion of the C<sub>2</sub>H hydrogen, the frequencies of the  $A_2$  vibrations are not affected by the C<sub>2</sub>-deuteration, while the vibrational frequencies of the other symmetry species are affected more or less. In the spectrum of Im<sup>-</sup>-2-d<sub>1</sub> (Fig. 2B), two Raman bands at 847 and 658 cm<sup>-1</sup> have no counterpart IR bands and they are definitely assigned to the  $A_2$  modes. Therefore, it is very likely that the missing  $A_2$  Raman band of Im<sup>-</sup>-d<sub>0</sub> is covered by the 846 cm<sup>-1</sup>  $B_2$  band.

For unsymmetrically deuterated isotopomers,  $Im^{-5-d_1}$  and  $-2,5-d_2$ , the symmetry reduces to  $C_s$  and the normal vibrations are classified into A' (in-plane) and A''(out-of-plane) species. Polarized Raman bands and their IR counterparts are exclusively assigned to A' modes. On the basis of the assignments for symmetrical isotopomers, the in-plane vibrations of the unsymmetrical isotopomers are expected to be above 800 cm<sup>-1</sup>. Accordingly a few IR bands above 800 cm<sup>-1</sup>, which do not have Raman counterparts, are also assigned to A' modes. The IR and/or Raman bands below 800 cm<sup>-1</sup> are assigned to A'' modes without doubt. An IR band around 840 cm<sup>-1</sup> in each spectrum of Im<sup>-</sup>-5- $d_1$  and -2,5- $d_2$  is also ascribed to an A'' mode (C<sub>4</sub>H wagging) with reference to the assignments for symmetrical isotopomers.

Figure 3 shows the IR and Raman spectra of 4-MeIm<sup>-</sup> and its deuterated isotopomers. Characteristic of 4-MeIm<sup>-</sup> are the vibrations of the methyl group attached to C<sub>4</sub>. The methyl group vibrations are not affected significantly by the deuteration in the Im<sup>-</sup> ring



Fig. 3. IR (upper) and Raman (lower) spectra of  $4-MeIm^--d_0$  (A),  $4-MeIm^--2-d_1$  (B),  $4-MeIm^--5-d_1$  (C),  $4-MeIm^--2, 5-d_2$  (D).

and can be identified easily: the degenerate deformation at ca 1440 cm<sup>-1</sup>, the symmetric deformation at  $ca 1385 \text{ cm}^{-1}$ , and the degenerate rocking at  $ca 980 \text{ cm}^{-1}$ . In addition to these C-H bending modes, the  $C_4$ -CH<sub>3</sub> stretching, deformation, and wagging modes are expected. One of the striking differences between the Raman spectra of  $Im^--d_0$  and 4-MeIm<sup>-</sup>- $d_0$  is the appearance of a strong band around 600 cm<sup>-1</sup> in the latter spectrum. This band is assigned to the  $C_4$ -CH<sub>3</sub> stretch. Two Raman bands around 350 and 275 cm<sup>-1</sup> are also characteristic of 4-MeIm<sup>-</sup> and they are assigned to the C<sub>4</sub>-CH<sub>3</sub> deformation and wagging modes, respectively. Similar deformation and wagging modes have been found at 334 and 320 cm<sup>-1</sup>, respectively, for *p*-cresol [19]. If the methyl hydrogen atoms are neglected, 4-MeIm<sup>-</sup> has C<sub>s</sub> symmetry. Accordingly, assignment of the IR and Raman bands due to the imidazolate ring vibrations can be made in a way similar to that adopted in assigning the IR and Raman bands of unsymmetrically deuterated Im<sup>-</sup>. One point to be noted is the occurrence of Fermi resonance in 4-MeIm<sup>-</sup>-2- $d_1$ . The doublet at 814 and 793  $cm^{-1}$  cannot be assigned to two fundamentals. We have ascribed the doublet to Fermi resonance between an A'' fundamental around 810 cm<sup>-1</sup> and the second overtone of the 272 cm<sup>-1</sup> A'' mode (3 × 272 = 816).

Using the fundamental frequencies determined experimentally for Im<sup>-</sup>, 4-MeIm<sup>-</sup>, and their deuterated isotopomers, we have made normal coordinate calculations in order to confirm the experimental assignments and to reveal the vibrational modes of the fundamentals. The force constants used in the normal coordinate calculations are listed in Table 2. The calculated fundamental frequencies are compared with the experimental ones in Tables 3 and 4. The average deviation of the calculated frequencies from experimental ones is 4.5 cm<sup>-1</sup> for 104 in-plane fundamentals and 3.8 cm<sup>-1</sup> for 43 out-of-plane fundamentals. The good agreement between the experimental and calculated frequencies supports the present assignments. Approximate descriptions of the calculated vibrational modes are also given in Tables 3 and 4. In presenting the vibrational modes of Im-, we use subscripts 's' and 'a' to denote symmetric and asymmetric combinations (with respect to the  $C_2$  rotation) of the internal coordinates indicated in the parentheses. For example,  $v_s(N_1C_2, N_3C_2)$  represents the symmetric stretch of the N<sub>1</sub>C<sub>2</sub> and N<sub>3</sub>C<sub>2</sub> bonds, while  $\nu_a(N_1C_2, N_3C_2)$  stands for the asymmetric stretch of the same bonds. Table 5 shows the frequencies of weak IR and/or Raman bands that are assignable to overtone, combination, or hot bands.

For Im<sup>-</sup>, strong Raman scattering arises from the following three  $A_1$  modes: the C<sub>4</sub>C<sub>5</sub> stretch [ $\nu$ C<sub>4</sub>C<sub>5</sub>], the symmetric stretch of the N<sub>1</sub>C<sub>2</sub>N<sub>3</sub> linkage [ $\nu_s$ (N<sub>1</sub>C<sub>2</sub>, N<sub>3</sub>C<sub>2</sub>)], and the symmetric stretch of the N<sub>1</sub>C<sub>5</sub> and N<sub>3</sub>C<sub>4</sub> bonds [ $\nu_s$ (N<sub>1</sub>C<sub>5</sub>, N<sub>3</sub>C<sub>4</sub>)] (see Table 3). These stretching modes do not largely couple with C-H (D) bending modes and, hence, the

No.	Coordinates involved*	Value <sup>†</sup>	Error‡
Stretch			
1 vCH	[	5.1900	
$2 v N_1 C$	$C_2$ , $\nu N_3 C_2$	8.5419	0.2838
$3 \nu N_1 C$	$C_5$ , $\nu N_3 C_4$	7.4393	0.2683
4 vC₄C	25	9.0888	0.3541
5 vC4C	CH₃	4.8430	0.1398
Bend			
6 ØNC	C <sub>2</sub> H	0.5177	0.0058
7 ØXC	C₄H, φXC₅H	0.4587	0.0046
8 ØNC	CC, ØNCN	1.4762	0.0443
9 ØCN	1C	1.9933	0.0713
10 øXC	C <sub>4</sub> CH <sub>3</sub>	0.5827	0.0232
Stretch/	stretch		
11 vNC	C/νCC (C common)	1.2744	0.1168
12 vNC	/νNC (C common)	1.3587	0.0604
13 vNC	$V/\nu NC$ (N common)	0.9068	0.0569
14 vNC	/vXC (N, C uncommon)	-1.1603	0.1425
15 vXC	$C_4/\nu C_4 CH_3$	0.0296	0.0536

Table 2. Valence force constants of the imidazolate ring

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Table 2. (Continued)

No.	Coordinates involved*	Value†	Error‡
Stre	nch/bend		
16 ·	$vNC_2/\phi NC_2H$ (N common)§	0.1037	0.0129
17 ·	$\nu NC_i / \phi NC_i H$ (N common, $i = 4$ or 5)§	0.1831	0.0119
18	vCC/øCCH§	0.0719	0.0135
19 ·	$\nu NC_2/\phi NC_i H$ (N common, $i = 4$ or 5)	0.0600	0.0170
20	$vNC_i/\phi NC_2H$ (N common, $i = 4$ or 5)	-0.0167	0.0107
21	vNC/ $\phi$ CCH (terminal C common)	-0.0056	0.0118
22	vXY/øXYZ	1.7581	0.1876
23	vXC₄/φXC₄CH₃§	-0.1189	0.0636
24	vC4CH3/øN3C4C5	-0.5976	0.0534
Ben	nd/bend		
25	$\phi CNC_2/\phi NC_2 H$ (N common)	-0.0586	0.0139
26	$\phi C_2 NC/\phi NCH (N, C \text{ common})$	0.0633	0.0098
27	$\phi \mathbf{NC}_i \mathbf{C}_i / \phi \mathbf{C}_i \mathbf{C}_i \mathbf{H} \ (i, j = 4 \text{ or } 5) \mathbf{\P}$	0.0268	0.0122
28	$\phi XC_i H/\phi YC_i H$ (i, j=4 or 5)**	0.0035	0.0028
29	$\phi NC_i H/\phi NC_2 H$ (N uncommon, $i = 4$ or 5) <sup>††</sup>	-0.0084	0.0018
30	φXYC₄/φYC₄CH₃¶	-0.1624	0.0733
Wa	gging		
31	πCH	0.2956	0.0826
32	$\pi C_4 CH_3$	0.4620	0.0242
Tor	sion		
33 ·	$\tau N_1 C_2$ , $\tau N_3 C_2$ , $\tau C_4 C_5$	0.1662	0.0188
34 ·	$\tau N_1 C_5, \tau N_3 C_4$	0.3060	
Wa	gging/wagging		
35	$\pi C_4 H / \pi C_2 H, \pi C_5 H / \pi C_2 H$	0.0836	0.0682
36	$\pi C_4 H / \pi C_5 H$	-0.0597	0.0288
37	$\pi C_5 H/\pi C_4 CH_3$	0.0050	0.0221
Wa	gging/torsion		
38	$\pi C_2 H / \tau N C_2 \ddagger \ddagger$	-0.0392	0.0340
39	$\pi \mathbf{C}_i \mathbf{H} / \tau \mathbf{X} \mathbf{C}_i \ (i = 4 \text{ or } 5) \ddagger \ddagger$	-0.0791	0.0323
40	$\pi CH/\tau XY$ (C is bonded with X)§§	0.1020	0.0538
41	$\pi C_4 CH_3 / \tau C_4 C_5 \ddagger$	-0.1013	0.0353
42	$\pi C_4 CH_3 / \tau N_3 C_4 \ddagger \ddagger$	-0.1527	0.0357
Tor	rsion/torsion		
43	rCN/rCX (adjacent torsional axis)	-0.1754	0.0087

\* Internal coordinates. Positions of nitrogen and carbon atoms are specified, when necessary. X, Y and Z stand for carbon or nitrogen atoms.

 $\dagger$  Units are mdyn Å<sup>-1</sup> for stretch-stretch interaction constants, mdyn rad<sup>-1</sup> for stretch-bend constants and mdyn Å rad<sup>-2</sup> for the others.

 $\ddagger$  Standard errors obtained in the least squares refinement of force constants. The constants for the CH stretch and the N<sub>1</sub>C<sub>5</sub>, N<sub>3</sub>C<sub>4</sub> torsions are fixed.

\$ This constant is used also for the interaction  $\nu XC/\phi YCR$  (X, Y = C or N; R = H or CH<sub>3</sub>), but the sign is reversed.

|| This constant is used also for the interaction  $\nu XY/\phi ZCH$  (Y is bonded with C; X, Y, Z = C or N) with its sign reversed.

¶ This constant is used also for the interaction  $\phi XYC/\phi ZCR$  (X, Y, Z=C or N; R=H or CH<sub>3</sub>) with its sign reversed.

\*\* When both X and Y are N or C, this constant is multiplied by -1.

†† This constant applies to the interactions of  $\phi N_1 C_2 H$  with  $\phi N_3 C_4 H$ and  $\phi C_4 C_5 H$ , but the sign is reversed for the interactions with  $\phi N_1 C_5 H$ and  $\phi C_5 C_4 H$ . When  $\phi N_3 C_2 H$  is involved, the sign is reversed for the interactions with  $\phi N_3 C_4 H$  and  $\phi C_4 C_5 H$ .

‡‡ This constant represents an interaction where X of  $\pi CX$  (X = H or CH<sub>3</sub>) moves in the same direction as in the torsional motion. When the directions are opposite to each other, the sign is reversed.

§§ This constant applies to the case where the central carbon atom of the wagging coordinate moves in the same direction as in the torsion. When the directions are opposite to each other, the sign is reversed.

v <sub>obs</sub> *	V <sub>calc</sub>	$\Delta \nu \dagger$	Assignment‡
			Im <sup>-</sup> - <i>d</i> <sub>0</sub>
A <sub>1</sub> 1456 37n	1460	-4	νC.C.+δ(C.H. C.H)
1249 w 100m	1245	4	$v_1(N_1C_2, N_2C_2)$
1142 m. 90p	1141	i	$v_{1}(N_{1}C_{1}, N_{2}C_{4})$
1099—, 16p	1091	8	$\delta_s(C_AH, C_sH) - \nu C_AC_s$
945 sh, 7p	954	-9	$\phi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3} - \delta_{s}(C_{4}H, C_{5}H)$
B			
1459 s, sh	1462	-3	$v_{a}(N_{1}C_{2}, N_{3}C_{2}) - \delta C_{2}H + v_{a}(N_{1}C_{5}, N_{3}C_{4}) - \delta_{a}(C_{4}H, C_{5}H)$
1306 w, 14dp	1305	1	$\delta_{a}(C_{4}H, C_{5}H) + \nu_{a}(N_{1}C_{2}, N_{3}C_{2}) - \nu_{a}(N_{1}C_{5}, N_{3}C_{4}) - \delta C_{2}H$
1225 m, —	1218	7	$v_{a}(N_{1}C_{2}, N_{3}C_{2}) + \delta C_{2}H - \delta_{a}(C_{4}H, C_{5}H) - v_{a}(N_{1}C_{5}, N_{3}C_{4})$
1080 vs, 4dp	1074	6	$\nu_{a}(N_{1}C_{5}, N_{3}C_{4}) + \delta_{a}(C_{4}H, C_{5}H)$
927 m, 2dp	935	-8	$\gamma_{a}(N_{1}C_{5}C_{4}, N_{3}C_{4}C_{5}) - \phi_{a}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4})$
$A_2$		_	
846, 5dp	846	0	$\pi_{\rm s}({\rm C_4H},{\rm C_5H})+\tau{\rm C_4C_5}$
658—, 2dp	655	3	$\tau_{s}(N_{1}C_{5}, N_{3}C_{4}) + \pi_{s}(C_{4}H, C_{5}H)$
B <sub>2</sub>	0.40	•	$(\mathbf{H} - (\mathbf{H} \mathbf{C} - \mathbf{N} \mathbf{C}))$
846 w, 5dp	843	3	$\pi C_2 H - \tau_a (N_1 C_2, N_3 C_2)$
783 m, 2dp	7/4	9	$\pi_{a}(C_{4}H, C_{5}H) = \tau_{a}(N_{1}C_{5}, N_{3}C_{4})$
689 m, —	689	U	$\tau_a(N_1C_2, N_3C_2)$
			$Im^{-}-2-d_{1}$
<i>A</i> <sub>1</sub>			
1461—, 64p	1460	1	$\nu C_4 C_5 + \delta_s (C_4 H, C_5 H)$
1223 m, 100p	1222	1	$\nu_{s}(N_{1}C_{2}, N_{3}C_{2}) - \nu_{s}(N_{1}C_{5}, N_{3}C_{4})$
1138 m, 94р	1136	2	$\nu_{\rm s}({\rm N}_1{\rm C}_5,{\rm N}_3{\rm C}_4)$
1064—, 4p	1087	-23	$\delta_{\rm s}({\rm C}_4{\rm H},{\rm C}_5{\rm H})-\nu{\rm C}_4{\rm C}_5$
935 w, 13p	938	-3	$\phi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3} - \delta_{s}(C_{4}H, C_{5}H)$
<i>B</i> <sub>1</sub>			
1425 vs, —	1424	1	$v_{a}(N_{1}C_{2}, N_{3}C_{2}) - o_{a}(C_{4}H, C_{5}H) + v_{a}(N_{1}C_{5}, N_{3}C_{4}) - oC_{2}D$
1294 m, —	1299	-5	$v_{a}(N_{1}C_{2}, N_{3}C_{2}) - v_{a}(N_{1}C_{5}, N_{3}C_{4}) + \delta_{a}(C_{4}H, C_{5}H)$
1091 w, 9dp	1117	-26	$v_{a}(N_{1}C_{5}, N_{3}C_{4}) + \delta_{a}(C_{4}H, C_{5}H)$
951 sh, 12dp	942	9	$\gamma_{a}(N_{1}C_{5}C_{4}, N_{3}C_{4}C_{5}) - \phi_{a}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4})$
86/s, 10p	8/4	-7	$\partial C_2 D$
8473dn	846	1	$\pi(C,H,C,H) + \pi C,C$
658— 3dp	655	3	$r_{s}(C_{4}H, C_{5}H) + r_{s}(C_{4}H, C_{5}H)$
B.	055	5	
785 m. —	784	1	$\pi_{4}(C_{4}H, C_{3}H) - \tau_{4}(N_{1}C_{5}, N_{3}C_{4}) - \pi C_{2}D$
744 vw. 9dp	740	4	$\pi C_{1}D + \pi_{1}(C_{1}H, C_{2}H)$
582 m, 2dp	577	5	$\tau_{a}(N_{1}C_{2}, N_{3}C_{2})$
•			$Im^{-4}, 5-d_2$
$A_1$			
1395—, 61p	1395	0	vC <sub>4</sub> C <sub>5</sub>
1242 w, 99p	1244	-2	$\nu_{\rm s}({\rm N}_{1}{\rm C}_{2},{\rm N}_{3}{\rm C}_{2})$
1117 w, 100p	1117	0	$\nu_{\rm s}({\rm N}_{1}{\rm C}_{5},{\rm N}_{3}{\rm C}_{4})$
979—, 7p	979	0	$\phi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3}$
778 w, 15p	773	5	$\delta_{\rm s}({\rm C_4D,C_5D})$
$B_1$	1 4 9 0	-	
1446 vs, 7dp	1439	7	$v_{a}(N_{1}C_{2}, N_{3}C_{2}) - oC_{2}H + v_{a}(N_{1}C_{5}, N_{3}C_{4})$
1250 sh, —	1247	3	$v_{a}(N_{1}C_{5}, N_{3}C_{4}) - v_{a}(N_{1}C_{2}, N_{3}C_{2})$
1185 s, 8dp	1184	1	$\sigma_{L_2\Pi} + \nu_a(N_1U_5, N_3U_4) - \sigma_a(U_4D, U_5D) + \nu_a(N_1U_2, N_3C_2)$
907 w, 70p	904	10	$\gamma_{a}(N_{1}\cup_{5}\cup_{4}, N_{3}\cup_{4}\cup_{5}) = \varphi_{a}(\bigcup_{2}N_{1}\cup_{5}, \bigcup_{2}N_{3}\cup_{4})$
oor iii,	0/1	10	$v_{a}(v_{4}v, v_{5}v) + v_{a}(v_{1}v_{5}, v_{3}v_{4})$
726 14dn	774	2	$\pi$ (C.D. C.D.)
	560	2	$t_1(N_1C_1, N_2C_1) - tC_1C_2 - \pi(C_1D_1C_2D_1)$
B <sub>2</sub>	200		(1,1,2,1,1,2,4) $(2,4,2,3,1,4,2,4,2,3,1,4,2,2,2,2,3,1,2,2,2,2,2,2,2,2,2,2,2,2,2,2$
~2 843 w. 1dn	842	1	лС-Н
692 w. —	689	3	$\tau_{a}(N_{1}C_{2}, N_{3}C_{2})$
594 w, 4dp	590	4	$\pi_{a}(C_{4}D, C_{5}D) - \tau_{a}(N_{1}C_{5}, N_{3}C_{4})$

# Table 3. Observed and calculated frequencies (in cm<sup>-1</sup>) of imidazolate and its deuterated compounds

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Table 3. (Continued)

$\nu_{obs}^{*}$	$\nu_{\rm calc}$	Δν†	Assignment‡
			Im <sup>-</sup> -2,4,5-d <sub>3</sub>
A1	1205	0	
1395—, 63p	1395	0	$\mathcal{M}_4 \mathcal{L}_5$
1220—, 85p	1219	1	$v_{s}(N_{1}C_{2}, N_{3}C_{2})$
1113 w, 100p	1115	-2	$\nu_{s}(N_{1}\cup_{5}, N_{3}\cup_{4})$
965 vw, 19p	958		$\varphi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3}$
779 w, 14p	112	1	$O_{\rm s}(\rm C_4D,\rm C_5D)$
<i>B</i> <sub>1</sub>		~	
1386 vs, —	1391	-5	$v_a(N_1C_2, N_3C_2)$
1245 w, 9dp	1240	5	$v_a(N_1C_5, N_3C_4) - v_a(N_1C_2, N_3C_2)$
937 vw, —	944	-7	$\partial C_2 D - \partial_a (C_4 D, C_5 D) + \gamma_a (N_1 C_5 C_4, N_3 C_4 C_5)$
905 vw, 3dp	902	3	$\gamma_{a}(N_{1}C_{5}C_{4}, N_{3}C_{4}C_{5}) - \varphi_{a}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) + o_{a}(C_{4}D, C_{5}D)$
832 s, 1dp	829	3	$\partial C_2 D + \partial_a (C_4 D, C_5 D) + \nu_a (N_1 C_5, N_3 C_4)$
$A_2$			
727—, 15dp	724	3	$\pi_{\rm s}({\rm C}_4{\rm D},{\rm C}_5{\rm D})$
	560		$\tau_{s}(N_{1}C_{5}, N_{3}C_{4}) - \tau C_{4}C_{5} - \pi_{s}(C_{4}D, C_{5}D)$
$B_2$			
748—, 3dp	750	-2	$\pi C_2 D$
611—, 8dp	608	3	$\pi_{a}(C_{4}D, C_{5}D) + \tau_{a}(N_{1}C_{2}, N_{3}C_{2}) - \tau_{a}(N_{1}C_{5}, N_{3}C_{4})$
564 m, —	558	6	$\tau_{a}(N_{1}C_{2}, N_{3}C_{2}) - \pi C_{2}D + \tau_{a}(N_{1}C_{5}, N_{3}C_{4}) - \pi_{a}(C_{4}D, C_{5}D)$
			$\mathrm{Im}^{-}$ -5- $d_{1}$
Α'			
1457 vs, 5p	1451	6	$v_a(N_1C_2, N_3C_2) - \delta C_2 H - \delta C_4 H + v_a(N_1C_5, N_3C_4)$
1427 w, 51p	1428	-1	$\nu C_4 C_5 + \nu_a (N_1 C_2, N_3 C_2) + \delta C_4 H$
1274 vw, 28p	1274	0	$v_{a}(N_{1}C_{5}, N_{3}C_{4}) - v_{a}(N_{1}C_{2}, N_{3}C_{2}) - \delta C_{4}H$
1243 w, 86p	1245	-2	$\nu_{s}(N_{1}C_{2}, N_{3}C_{2})$
1215 m, —	1209	6	$\delta C_2 H + \nu_a (N_1 C_2, N_3 C_2) - \delta C_4 H$
1131 w, 100p	1131	0	$\nu_{\rm s}({\rm N}_{1}{\rm C}_{5},{\rm N}_{3}{\rm C}_{4})$
1081 s, 20p	1076	5	$\nu_{a}(N_{1}C_{5}, N_{3}C_{4}) + \delta C_{4}H$
968 w, 8p	971	-3	$\phi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3}$
918 m, 8p	917	1	$\gamma_{a}(N_{1}C_{5}C_{4}, N_{3}C_{4}C_{5}) - \phi_{a}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4})$
822 w, 21p	817	5	δC₅D
A"			
848 w, —	843	5	$\pi C_2 H - \tau_a (N_1 C_2, N_3 C_2)$
823 w, —	817	6	πC₄H
688—, 7dp	689	-1	$\tau_{a}(N_{1}C_{2}, N_{3}C_{2})$
681m, —	684	-3	$\pi C_5 D$
571 w, 6dp	573	-2	$\pi C_5 D - \tau_s (N_1 C_5, N_3 C_4) + \tau C_4 C_5 - \tau_a (N_1 C_5, N_3 C_4)$
			$Im^{-}-2,5-d_{2}$
A'			
1439 w, 41p	1433	6	$vC_4C_5 + \delta C_4H$
1390 vs, —	1401	-11	$\nu_{a}(N_{1}C_{2}, N_{3}C_{2}) + \nu_{a}(N_{1}C_{5}, N_{3}C_{4}) + \nu C_{4}C_{5} - \delta C_{2}D$
1275 vw, 7p	1274	1	$v_{a}(N_{1}C_{5}, N_{3}C_{4}) - v_{a}(N_{1}C_{2}, N_{3}C_{2}) - \delta C_{4}H$
1222 w, 72p	1220	2	$v_{s}(N_{1}C_{2}, N_{3}C_{2}) - v_{s}(N_{1}C_{5}, N_{3}C_{4})$
1127 w, 100p	1131	-4	$\nu_{\rm s}({\rm N}_{\rm 1}{\rm C}_{\rm 5},{\rm N}_{\rm 3}{\rm C}_{\rm 4})$
1114 w. —	1098	16	$v_{a}(N_{1}C_{5}, N_{3}C_{4}) + \delta C_{4}H - v_{s}(N_{1}C_{5}, N_{3}C_{4})$
968—, 5p	956	12	$\phi_{s}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) - \gamma N_{1}C_{2}N_{3}$
935—, 10p	933	2	$\gamma_{a}(N_{1}C_{5}C_{4}, N_{3}C_{4}C_{5}) - \phi_{a}(C_{2}N_{1}C_{5}, C_{2}N_{3}C_{4}) + \delta C_{2}D$
881 m. 3p	878	3	$\delta C_2 D - \gamma_a (N_1 C_5 C_4, N_3 C_4 C_5)$
811 m, 6p	808	3	δC <sub>5</sub> D
A" .			
832 w. —	819	13	πC₄H
747—, 3dp	749	-2	$\pi C_2 D + \tau_a (N_1 C_5, N_3 C_4)$
689 w. 3dp	684	5	$\pi C_{5}D$
	591		$\tau_{a}(N_{1}C_{2}, N_{3}C_{2}) + \pi C_{5}D - \pi C_{2}D$
563 w,	558	5	$r_{a}(N_{1}C_{2}, N_{3}C_{2}) - \pi C_{2}D - \pi C_{5}D$

\* Frequencies followed by IR intensities (vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder) and relative Raman intensities (100 for the strongest band) together with polarization properties (p, polarized; dp, depolarized).

 $\dagger \Delta \nu = \nu_{\rm obs} - \nu_{\rm calc} \, .$ 

‡ Approximate descriptions of the calculated modes.

# Vibrational analysis of the imidazolate ring

Table 4.	Observed and calculated frequencies (in cm <sup>-1</sup> ) of 4-methylimidazolate and
	its deuterated compounds

$\nu_{obs}^{*}$	$\nu_{\rm calc}$	$\Delta \nu \dagger$	Assignment‡
			4-MeIm <sup>-</sup> -d <sub>0</sub>
4' 1522 w 20-	1524	1	
1333 w, 29p	1550	5	CH deg deform
1439—, 18p	1/35	3	$\delta C_1 H \pm v N_1 C_1 = v N_1 C_1 = v C_1 C_1 \pm v N_1 C_2$
384 w 14n		5	$CH_2$ sym deform
1299 w. 14n	1303	-4	$vN_{1}C_{1} + vN_{1}C_{2} - vN_{2}C_{2} - vC_{4}C_{4}$
256 w. 100p	1254	2	$\nu N_3 C_3 + \nu N_1 C_2 - \delta C_5 H$
232 sh. 39p	1233	-1	$\nu N_1 C_5 - \nu N_1 C_2 - \delta C_5 H$
217 m. —	1210	7	$\delta C_2 H - \nu N_3 C_2 - \delta C_5 H$
1105 s, 22p	1096	9	$\nu N_1 C_5 + \delta C_5 H$
1009 m, 22p	1021	-12	$\phi C_2 N_3 C_4 - \nu N_3 C_4 - \gamma N_3 C_4 C_5 - \nu C_4 C H_3 - \gamma N_1 C_2 N_3$
977 w, —	—		CH <sub>3</sub> rock
949 m, 5p	953	-4	$\phi C_2 N_1 C_5 - \gamma N_1 C_2 N_3 - \gamma N_1 C_5 C_4$
663 w, 65	665	-2	$\nu C_4 CH_3 - \gamma N_3 C_4 C_5 + \nu N_3 C_4$
350—, 10	349	1	δC₄CH <sub>3</sub>
A″			
1439—, 18	_		CH <sub>3</sub> deg. deform.
977 w, —	—		CH <sub>3</sub> rock
836 m, —	843	-7	$\pi C_2 H$
790 m, —	808	-18	$\pi C_5 H + \tau N_1 C_5$
668 m, —	690	-2	$\tau N_1 C_2 - \tau N_3 C_2$
	656		$\pi C_4 CH_3 + \tau N_1 C_5$
275—, 14	276	-1	$\pi C_4 CH_3 - \tau N_3 C_4$
			4-MeIm <sup>-</sup> -2- $d_1$
A'			
1532 w, 41p	1533	-1	$\nu C_4 C_5 - \nu C_4 C H_3 + \delta C_5 H$
1443 w, 16p		_	CH <sub>3</sub> deg. deform.
1392 vs, —	1397	-5	$\nu N_3 C_2 - \nu N_1 C_2 + \nu N_3 C_4 - \nu C_4 C_5 + \delta C_2 D$
1384—, 26p	1200		$CH_3$ sym. deform.
1298 w, 6p	1299	-1	$vN_{3}C_{4} - vN_{3}C_{2} + vN_{1}C_{2}$
1243 W, 70p	1243	1	$\partial C_5 H = \nu N_1 C_5 = \nu N_3 C_2 + \nu C_4 C H_3$
1215 m, 100p	1214	1	$\nu \mathbf{N}_1 \mathbf{C}_2 = \nu \mathbf{N}_1 \mathbf{C}_5 + \nu \mathbf{N}_3 \mathbf{C}_2 = \nu \mathbf{N}_1 \mathbf{C}_2 \mathbf{N}_3$
1021 m 44n	1020	11	$\frac{\partial N_1 C_5 + \partial C_5 \Pi}{\partial C_1 + \partial N_1 C_2 + \partial C_2 C_2 + \partial C_2 C_2 + \partial C_2 C_2 + \partial C_2 C_2 + \partial$
094 m	1020	11	$\varphi C_2 r_3 C_5 = \rho r_3 C_4 - \rho r_3 C_4 C_5 - \rho C_4 C r_3 - \rho r_1 C_2 r_3$
964 w, — 953 w 15n	942	11	$\phi$ C-N.C. = $v$ N.C.N. = $v$ N.C.C.
869 s —	892	-23	$\delta C_{2} D$
663 m 80	661	-2	$\nu C_1 C H_2 = \nu N_2 C_1 C_2 + \nu N_2 C_4$
346—, 12	345	1	δC/CH
A"		-	· - 4 5
1443 w, 16	_		CH <sub>3</sub> deg. deform.
984 w, —			CH <sub>3</sub> rock
814 m, —)			
793 m. — <sup>8</sup>	810	<b>−7</b> ∥	$\pi C_{5}H + \tau N_{1}C_{5}$
742 vw	747	-5	πC <sub>2</sub> D
<u> </u>	657	5	$\pi C_{4}CH_{3}$
582 m. —	582	0	$\pi C_1 D - \tau N_1 C_2 + \tau N_2 C_2$
272—, 19	271	1	$\pi C_4 C H_3 - \tau N_3 C_4$
,		-	4 MaIm <sup>-</sup> 5 d
A'			+-wickill -J-41
1512 w, 46p	1511	1	$\nu C_4 C_5 - \nu C_4 CH_3$
1440—, 28p			CH <sub>3</sub> deg. deform.
1439 vs, —	1428	11	$\delta C_2 H + \nu N_3 C_2 - \nu N_1 C_2 - \nu C_4 C_5$
1383 vm, 21p	—		CH <sub>3</sub> sym. deform.
1299 w, —	1299	0	$\nu N_3 C_4 + \nu N_1 C_2$
1240 sh, 100p	1245	-5	$\nu N_3 C_2 + \nu N_1 C_2$
1233 m, —	1224	-1	$vN_1C_5 - vN_1C_2 + vN_3C_2 - \delta C_2H$
1173 s, 26p	1170	3	$\nu N_1 C_5 + \partial C_2 H - \partial C_5 D$
1012 w, 56p	1014	-2	$\varphi \cup_2 N_3 \cup_5 - \gamma N_3 \cup_4 \cup_5 - \nu \cup_4 \cup H_3 - \gamma N_1 \cup_2 N_3 - \nu N_3 \cup_4 \cup_5 - \nu \cup_5 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6 \cup_6$
980 m, 2			CH <sub>3</sub> rock

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Table 4. (Continued)

₽ <sub>obs</sub> *	$\nu_{\rm calc}$	$\Delta v^{\dagger}$	Assignment‡
956 w, 8p	960	-4	$\phi C_2 N_1 C_5 - \gamma N_1 C_2 N_3 - \gamma N_1 C_5 C_4 + \nu N_1 C_5$
836 m, 6	837	-1	δC₅D
659 w, 50	657	2	$\nu C_4 CH_3 - \gamma N_3 C_4 C_5 + \nu N_3 C_4$
342, 11	342	0	δC <sub>4</sub> CH <sub>3</sub>
A"			
1440, 28	_		CH <sub>3</sub> deg. deform.
986 m, 2			CH <sub>3</sub> rock
836 m, 6	842	-6	$\pi C_2 H$
687 m, 13	691	-4	$\pi C_5 D + \tau N_1 C_2$
687 m, 13	687	0	$\pi C_4 CH_3 - \pi C_5 D$
567 m,	576	-9	$\tau N_1 C_5 + \pi C_5 D + \pi C_4 C H_3 - \tau C_4 C_5$
278—, 18	274	4	$\pi C_4 CH_3 - \tau N_3 C_4$
A'			4-MeIm <sup>-</sup> -2,5- $d_2$
1512.vw. 40m	1506	6	$\nu C_{4}C_{5} - \nu C_{4}CH_{2}$
1441 w. –	_	Ŭ	CH <sub>2</sub> deg. deform.
1392 vs. —	1389	3	$\nu N_3 C_3 = \nu N_1 C_3 + \nu N_3 C_4 - \nu C_4 C_5 + \delta C_3 D$
1379—, 20p	_	_	CH <sub>2</sub> svm. deform.
1298 w. —	1296	2	$\nu N_{3}C_{4} + \nu N_{1}C_{2} - \nu N_{3}C_{2}$
1221 m, 100p	1216	5	$\nu N_3 C_2 + \nu N_1 C_2$
1202 m, 20p	1200	2	$\nu N_1 C_5$
1015 m, 47p	1014	1	$\phi C_2 N_3 C_5 - \gamma N_3 C_4 C_5 - \nu C_4 C H_3 - \nu N_3 C_4 - \nu N_1 C_5$
986 vw, —	_		CH <sub>3</sub> rock
955 vw, —	961	-6	$\phi C_2 N_1 C_5 - \gamma N_1 C_2 N_3 - \delta C_2 D$
901 m, —	894	7	$\delta C_2 D$
816 s, —	831	-15	δC <sub>5</sub> D
655 w, 73	652	3	$\nu C_4 CH_3 - \gamma N_3 C_4 C_5 + \nu N_3 C_4$
339—, 18	339	0	δC₄CH <sub>3</sub>
A"			
1441 w, —			CH <sub>3</sub> deg. deform.
986 vw, —			CH <sub>3</sub> rock
	748		$\pi C_2 D$
695 w, —	688	7	$\pi C_5 D - \pi C_4 C H_3$
	602		$\pi C_5 D + \pi C_4 C H_3 - \tau N_3 C_2 - \pi C_2 D$
558 m, —	557	1	$\tau N_1 C_5 + \pi C_5 D + \pi C_2 D - \tau N_1 C_2$
268—, 16	270	-2	$\pi C_4 CH_3 - \tau N_3 C_4$

\* Frequencies followed by IR intensities (vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder) and relative Raman intensities (100 for the strongest band) together with polarization properties (p, polarized; dp, depolarized).

 $\dagger \Delta \nu = \nu_{\rm obs} - \nu_{\rm calc} \, .$ 

‡ Approximate descriptions of the calculated modes.

§ Doublet due to Fermi resonance.

 $\|$  Difference between the mean frequency of the doublet and the calculated one.

pattern of frequency shift upon deuteration is rather simple. The  $\nu C_4 C_5$  frequency decreases from 1456 to 1427 cm<sup>-1</sup> upon deuteration at C<sub>4</sub> and further to 1395 cm<sup>-1</sup> upon additional deuteration at C<sub>5</sub>. Deuteration at C<sub>2</sub> does not affect the frequency significantly. This is also the case for  $\nu_s(N_1C_5, N_3C_4)$ , which appears at 1142 cm<sup>-1</sup> for Im<sup>-</sup>- $d_0$ . Conversely, the  $\nu_s(N_1C_2, N_3C_2)$  mode at 1249 cm<sup>-1</sup> in Im<sup>-</sup>- $d_0$  shows about 20 cm<sup>-1</sup> downshift upon C<sub>2</sub>-deuteration but is insensitive to the C<sub>4</sub>,C<sub>5</sub>-deuteration. The lack of coupling of the strongly Raman active modes with C-H (D) bending modes lends a common feature to the Raman spectra of all isotopomers of Im<sup>-</sup>, that is, one strong band in the 1460–1390 cm<sup>-1</sup> region and two strong bands in the 1250–1110 cm<sup>-1</sup> region (see Fig. 2). In sharp contrast to the Raman spectra, the IR spectral features change drastically with deuteration. Strong IR bands such as those at 1459 and 1080 cm<sup>-1</sup> in the Im<sup>-</sup>- $d_0$  spectrum mostly arise from  $B_1$  modes and they are coupled with C-H (D) bending modes as seen in Table 3. The coupling scheme and the potential energy distribution are affected more or less by deuteration and so is the IR spectral pattern.

$Im^{-}-d_{0}$ $Im^{-}-d_{0}$ $I505 IR = 846 (A_{2}) + 658 (A_{2})$ $I373 IR, R = 689 (B_{2}) \times 2$ $I175 R = 1225 (B_{1}) + 658 (A_{2}) - 689 (B_{2})$ $Im^{-}-2-d_{1}$ $I424 R = 847 (A_{2}) + 582 (B_{2})$ $I329 R = 744 (B_{2}) + 582 (B_{2})$ $I231 R = 658 (A_{2}) + 582 (B_{2})$ $Im^{-}-4,5-d_{2}$ $I077 IR = 907 (B_{1}) + 726 (A_{2}) - 560^{\dagger} (A_{2})$ $Im^{-}-2,4,5-d_{3}$ $I492 R = 748 (B_{2}) \times 2$ $I454 R = 727 (A_{2}) \times 2$ $I310 R = 748 (B_{2}) + 564 (B_{2})$ $I287 R = 727 (A_{2}) + 564 (B_{2})$ $I077 IR = 790 (A'') + 275 (A'')$ $4-MeIm^{-}-2-d_{1}$ $I323 IR = 663 (A') \times 2, 742 (A'') + 582 (A'')$ $I173 IR = 582 (A'') \times 2$ $I016 IR = 742 (A'') + 272 (A'')$ $900 IR = 272 (A'') \times 2$ $I016 IR = 742 (A'') + 268 (A'')$ $I261 IR = 986 (A') + 268 (A'')$ $I242 IR = 901 (A') + 339 (A'') \times 2$		$\nu_{obs}^{*}$	Assignment
$ \begin{array}{c} 1505 \ \mathrm{IR} & 846 \ (A_2) + 658 \ (A_2) \\ 1373 \ \mathrm{IR}, \mathbf{R} & 689 \ (B_2) \times 2 \\ 1175 \ \mathbf{R} & 1225 \ (B_1) + 658 \ (A_2) - 689 \ (B_2) \end{array} \\ \mathrm{Im}^{-2-d_1} & \\ 1424 \ \mathbf{R} & 847 \ (A_2) + 582 \ (B_2) \\ 1329 \ \mathbf{R} & 744 \ (B_2) + 582 \ (B_2) \\ 1231 \ \mathbf{R} & 658 \ (A_2) + 582 \ (B_2) \\ 1231 \ \mathbf{R} & 658 \ (A_2) + 582 \ (B_2) \\ 1231 \ \mathbf{R} & 658 \ (A_2) + 582 \ (B_2) \\ \mathrm{Im}^{-4,5-d_2} & \\ \mathrm{Im}^{2,4,5-d_3} & \\ 1492 \ \mathbf{R} & 748 \ (B_2) \times 2 \\ 1454 \ \mathbf{R} & 727 \ (A_2) \times 2 \\ 1310 \ \mathbf{R} & 748 \ (B_2) + 564 \ (B_2) \\ 1287 \ \mathbf{R} & 727 \ (A_2) + 564 \ (B_2) \\ 1287 \ \mathbf{R} & 727 \ (A_2) + 564 \ (B_2) \\ 1287 \ \mathbf{R} & 727 \ (A_2) + 564 \ (B_2) \\ 4-\mathrm{MeIm}^{-}-d_0 & \\ \mathrm{In} & 1077 \ \mathrm{IR} & 790 \ (A'') + 275 \ (A''') \\ 4-\mathrm{MeIm}^{-}-2-d_1 & \\ & 1323 \ \mathrm{IR} & 663 \ (A') \times 2, 742 \ (A'') + 582 \ (A'') \\ 1173 \ \mathrm{IR} & 582 \ (A'') \times 2 \\ 1016 \ \mathrm{IR} & 742 \ (A'') + 272 \ (A''') \\ 900 \ \mathrm{IR} & 272 \ (A'') \times 2 \\ 4-\mathrm{MeIm}^{-}-2, 5-d_2 & \\ & 1482 \ \mathrm{IR} & 1221 \ (A') + 268 \ (A'') \\ 1261 \ \mathrm{IR} & 986 \ (A') + 268 \ (A'') \\ 1242 \ \mathrm{IR} & 901 \ (A') + 339(A'') , 558 \ (A') + 339 \ (A'') \times 2 \end{array}$	$\overline{\mathrm{Im}^{-}}$ - $d_0$		
$\begin{array}{c} 1373 \ \mathrm{IR}, \ \mathrm{R}  689 \ (B_2) \times 2 \\ 1175 \ \mathrm{R}  1225 \ (B_1) + 658 \ (A_2) - 689 \ (B_2) \end{array}$ $\operatorname{Im}^{-2-d_1} \qquad \qquad$		1505 IR	846 $(A_2)$ + 658 $(A_2)$
$I175 R I225 (B_1) + 658 (A_2) - 689 (B_2)$ $Im^{-}2-d_1 I225 (B_1) + 658 (A_2) - 689 (B_2)$ $I424 R 847 (A_2) + 582 (B_2)$ $I329 R 744 (B_2) + 582 (B_2)$ $I231 R 658 (A_2) + 582 (B_2)$ $Im^{-}4,5-d_2 I077 IR 907 (B_1) + 726 (A_2) - 560^{\dagger} (A_2)$ $Im^{-}2,4,5-d_3 I492 R 748 (B_2) \times 2$ $I454 R 727 (A_2) \times 2$ $I310 R 748 (B_2) + 564 (B_2)$ $I287 R 727 (A_2) + 564 (B_2)$ $I173 IR 582 (A'') \times 2, 742 (A'') + 582 (A'')$ $I173 IR 582 (A'') \times 2$ $I016 IR 742 (A'') + 272 (A'')$ $900 IR 272 (A'') \times 2$ $I016 IR 742 (A'') + 272 (A'')$ $900 IR 272 (A'') \times 2$ $I482 IR 1221 (A') + 268 (A'')$ $I261 IR 986 (A') + 268 (A'')$ $I242 IR 901 (A') + 339 (A'') + 539 (A'') \times 2$		1373 IR, R	$689 (B_2) \times 2$
$Im^{-}2-d_{1}$ $1424 R = 847 (A_{2}) + 582 (B_{2})$ $1329 R = 744 (B_{2}) + 582 (B_{2})$ $1231 R = 658 (A_{2}) + 582 (B_{2})$ $Im^{-}4,5-d_{2} = 1077 IR = 907 (B_{1}) + 726 (A_{2}) - 560^{\dagger} (A_{2})$ $Im^{-}2,4,5-d_{3} = 1492 R = 748 (B_{2}) \times 2$ $1454 R = 727 (A_{2}) \times 2$ $1310 R = 748 (B_{2}) + 564 (B_{2})$ $1287 R = 727 (A_{2}) + 564 (B_{2})$ $1287 R = 727 (A_{2}) + 564 (B_{2})$ $4-MeIm^{-}-d_{0} = 1077 IR = 790 (A'') + 275 (A'')$ $4-MeIm^{-}-2-d_{1} = 1323 IR = 663 (A') \times 2, 742 (A'') + 582 (A'')$ $1173 IR = 582 (A'') \times 2$ $1016 IR = 742 (A'') + 272 (A'')$ $900 IR = 272 (A'') \times 2 + 346 (A')$ $558 IR = 272 (A'') \times 2$ $4-MeIm^{-}-2,5-d_{2} = 1482 IR = 1221 (A') + 268 (A'')$ $1261 IR = 986 (A') + 268 (A'')$ $1242 IR = 901 (A') + 339 (A'') \times 25$		1175 R	$1225 (B_1) + 658 (A_2) - 689 (B_2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Im^{-}-2-d_{1}$		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1424 R	847 $(A_2)$ + 582 $(B_2)$
$1231 R = 658 (A_2) + 582 (B_2)$ $Im^{-}4,5-d_2 = 1077 IR = 907 (B_1) + 726 (A_2) - 560^{+} (A_2)$ $Im^{-}2,4,5-d_3 = 1492 R = 748 (B_2) \times 2 = 1454 R = 727 (A_2) \times 2 = 1310 R = 748 (B_2) + 564 (B_2) = 1287 R = 727 (A_2) + 564 (B_2) = 1287 R = 727 (A_2) + 564 (B_2)$ $4-MeIm^{-}-d_0 = 1077 IR = 790 (A'') + 275 (A'') = 1323 IR = 663 (A') \times 2, 742 (A'') + 582 (A'') = 1173 IR = 582 (A'') \times 2 = 1016 IR = 742 (A'') + 272 (A'') = 900 IR = 272 (A'') \times 2 = 1482 IR = 1221 (A') + 268 (A'') = 558 IR = 272 (A'') \times 2 = 1482 IR = 1221 (A') + 268 (A'') = 1261 IR = 986 (A') + 268 (A'') = 558 (A'') + 339 (A'') \times 2 = 1016 IR = 742 (A'') = 1242 IR = 901 (A') + 339 (A'') \times 2 = 1261 IR = 986 (A') + 268 (A'') = 558 (A'') + 339 (A'') \times 2 = 1242 IR = 901 (A') + 339 (A'') \times 2 = 1241 IR = $		1329 R	$744 (B_2) + 582 (B_2)$
$Im^{-}4,5-d_{2}$ $Im^{-}-2,4,5-d_{3}$ $I492 R 748 (B_{2}) \times 2$ $I454 R 727 (A_{2}) \times 2$ $I454 R 727 (A_{2}) \times 2$ $I310 R 748 (B_{2}) + 564 (B_{2})$ $I287 R 727 (A_{2}) + 564 (B_{2})$ $I287 R 727 (A_{2}) + 564 (B_{2})$ $I287 R 727 (A_{2}) + 564 (B_{2})$ $I077 IR 790 (A'') + 275 (A'')$ $4-MeIm^{-}-2-d_{1}$ $I323 IR 663 (A') \times 2, 742 (A'') + 582 (A'')$ $I173 IR 582 (A'') \times 2$ $I016 IR 742 (A'') + 272 (A'')$ $900 IR 272 (A'') \times 2 + 346 (A')$ $558 IR 272 (A'') \times 2$ $I482 IR 1221 (A') + 268 (A'')$ $I261 IR 986 (A') + 268 (A'')$ $I242 IR 901 (A') + 339(A'') + 539 (A'') \times 2$		1231 R	$658(A_2) + 582(B_2)$
$1077 \text{ IR} \qquad 907 (B_1) + 726 (A_2) - 560^{\dagger} (A_2)$ $Im^{-}-2,4,5-d_3 \qquad \qquad 1492 \text{ R} \qquad 748 (B_2) \times 2 \\ 1454 \text{ R} \qquad 727 (A_2) \times 2 \\ 1310 \text{ R} \qquad 748 (B_2) + 564 (B_2) \\ 1287 \text{ R} \qquad 727 (A_2) + 564 (B_2) \\ 4-\text{MeIm}^{-}-d_0 \qquad \qquad$	$Im^{-}-4,5-d_{2}$		
$Im^{-}2,4,5-d_{3}$ $I492 R 748 (B_{2}) \times 2$ $I454 R 727 (A_{2}) \times 2$ $I310 R 748 (B_{2}) + 564 (B_{2})$ $I287 R 727 (A_{2}) + 564 (B_{2})$ $I287 R 727 (A_{2}) + 564 (B_{2})$ $I077 IR 790 (A'') + 275 (A'')$ $4-MeIm^{-}2-d_{1}$ $I323 IR 663 (A') \times 2, 742 (A'') + 582 (A'')$ $I173 IR 582 (A'') \times 2$ $I016 IR 742 (A'') + 272 (A'')$ $900 IR 272 (A'') \times 2 + 346 (A')$ $558 IR 272 (A'') \times 2$ $I482 IR 1221 (A') + 268 (A'')$ $I261 IR 986 (A') + 268 (A'')$ $I242 IR 901 (A') + 339 (A'') \times 2$	· -	1077 IR	907 $(B_1)$ + 726 $(A_2)$ - 560† $(A_2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$Im^{-}-2,4,5-d_{3}$		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1492 R	748 $(B_2) \times 2$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		1454 R	$727(A_2) \times 2$
$1287 \text{ R}  727 (A_2) + 564 (B_2)$ 4-MeIm <sup>-</sup> -d <sub>0</sub> $1077 \text{ IR}  790 (A'') + 275 (A'')$ 4-MeIm <sup>-</sup> -2-d <sub>1</sub> $1323 \text{ IR}  663 (A') \times 2, 742 (A'') + 582 (A'')$ $1173 \text{ IR}  582 (A'') \times 2$ $1016 \text{ IR}  742 (A'') + 272 (A'')$ $900 \text{ IR}  272 (A'') \times 2 + 346 (A')$ $558 \text{ IR}  272 (A'') \times 2$ 4-MeIm <sup>-</sup> -2,5-d <sub>2</sub> $1482 \text{ IR}  1221 (A') + 268 (A'')$ $1261 \text{ IR}  986 (A') + 268 (A'')$ $1242 \text{ IR}  901 (A') + 339 (A'') \times 558 (A'') + 339 (A'') \times 2$		1310 R	$748 (B_2) + 564 (B_2)$
4-MeIm <sup>-</sup> - $d_0$ 1077 IR 790 (A") + 275 (A") 4-MeIm <sup>-</sup> -2- $d_1$ 1323 IR 663 (A') × 2, 742 (A") + 582 (A") 1173 IR 582 (A") × 2 1016 IR 742 (A") + 272 (A") 900 IR 272 (A") × 2 + 346 (A') 558 IR 272 (A") × 2 4-MeIm <sup>-</sup> -2,5- $d_2$ 1482 IR 1221 (A') + 268 (A") 1261 IR 986 (A') + 268 (A") 1242 IR 901 (A') + 339(A"), 558 (A') + 339 (A") × 2		1287 R	$727(A_2) + 564(B_2)$
$4-\text{MeIm}^{-2-d_1}$ $4-\text{MeIm}^{-2-d_1}$ $1323 \text{ IR} 663 (A') \times 2, 742 (A'') + 582 (A'')$ $1173 \text{ IR} 582 (A'') \times 2$ $1016 \text{ IR} 742 (A'') + 272 (A'')$ $900 \text{ IR} 272 (A'') \times 2 + 346 (A')$ $558 \text{ IR} 272 (A'') \times 2$ $4-\text{MeIm}^{-2}, 5-d_2$ $1482 \text{ IR} 1221 (A') + 268 (A'')$ $1261 \text{ IR} 986 (A') + 268 (A'')$ $1242 \text{ IR} 901 (A') + 339 (A'') + 539 (A'') \times 2$	4-MeIm <sup>-</sup> - $d_0$		
4-MeIm <sup>-</sup> -2- $d_1$ 1323 IR 1323 IR 1221 (A') × 2, 742 (A'') + 582 (A'') 1016 IR 122 (A'') × 2 1016 IR 122 (A'') + 268 (A'') 124 IR 124 IR 124 IR 124 (A'') + 339 (A'') + 339 (A'') × 2 124 IR 124 IR 124 IR 124 IR 124 (A'') + 339 (A'') + 339 (A'') × 2 124 IR 124 IR 12	v	1077 IR	790 ( <i>A</i> ") + 275 ( <i>A</i> ")
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$4-MeIm^{-}-2-d_{1}$		
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$		1323 IR	$663 (A') \times 2,742 (A'') + 582 (A'')$
$1016 \text{ IR}  742 (A'') + 272 (A'') \\900 \text{ IR}  272 (A'') \times 2 + 346 (A') \\558 \text{ IR}  272 (A'') \times 2 \\4-\text{MeIm}^{-2}, 5-d_2                                     $		1173 IR	582 (A") × 2
900 IR 272 $(A'') \times 2 + 346 (A')$ 558 IR 272 $(A'') \times 2$ 4-MeIm <sup>-</sup> -2,5-d <sub>2</sub> 1482 IR 1221 $(A') + 268 (A'')$ 1261 IR 986 $(A') + 268 (A'')$ 1242 IR 901 $(A') + 339 (A'') \times 558 (A') + 339 (A'') \times 2$		1016 IR	742 $(A'')$ + 272 $(A'')$
$558 \text{ IR} 272 (A'') \times 2$ 4-MeIm <sup>-</sup> -2,5-d <sub>2</sub> $1482 \text{ IR} 1221 (A') + 268 (A'')$ 1261 IR 986 (A') + 268 (A'') 1242 IR 901 (A') + 339(A'') + 339 (A'') \times 2		900 IR	$272(A'') \times 2 + 346(A')$
4-MeIm <sup>2,5-d<sub>2</sub> 1482 IR 1221 (A') + 268 (A") 1261 IR 986 (A') + 268 (A") 1242 IR 901 (A') + 339(A"), 558 (A') + 339 (A") × 2</sup>		558 IR	$272(A'') \times 2$
1482 IR 1221 $(A') + 268 (A'')$ 1261 IR 1266 $(A') + 268 (A'')$ 1242 IR 1242 IR 1242 IR 1242 IR 1242 IR 1242 IR 1242 IR 1242 IR 1242 $(A') + 339 (A'') + 339 (A''$	4-MeIm <sup>-</sup> -2.5- $d_{2}$		· · /
1261 IR 986 $(A')$ + 268 $(A'')$ 1242 IR 901 $(A')$ + 339 $(A'')$ + 558 $(A')$ + 339 $(A'')$ × 2		1482 IR	1221(A') + 268(A'')
1242 IR 901 $(A') + 339(A''), 558(A') + 339(A'') \times 2$		1261 IR	986 $(\dot{A}')$ + 268 $(\dot{A}'')$
		1242 IR	$901(A') + 339(A''), 558(A') + 339(A'') \times 2$

 Table 5. Combination and overtone frequencies (in cm<sup>-1</sup>) of imidazolate and

 4-methylimidazolate

\* IR and R denote IR and Raman frequencies, respectively.

† Calculated frequency.

The methyl substitution at C4 causes substantial changes in the normal modes (see Table 4). The C<sub>4</sub>-CH<sub>3</sub> stretch mixes with  $\nu$ C<sub>4</sub>C<sub>5</sub> and pushes the frequency upward to  $1533 \text{ cm}^{-1}$  in 4-MeIm<sup>-</sup>- $d_0$  and to  $1512 \text{ cm}^{-1}$  in 4-MeIm<sup>-</sup>-5- $d_1$  and  $-2,5-d_2$ . This mixed mode gives a strong and polarized Raman band. The strongest Raman band of 4-MeIm<sup>-</sup>- $d_0$  is observed at 1256 cm<sup>-1</sup> and this band is calculated to be due to an in-phase combination of  $\nu N_1C_2$  and  $\nu N_3C_2$  with a significant contribution from  $\delta C_3H$ . Another strong Raman band at 1232 cm<sup>-1</sup> is ascribed to an out-of-phase combination of  $\nu N_1C_2$ and  $\nu N_1 C_5$ . Deuteration at C<sub>2</sub> of 4-MeIm<sup>-</sup> changes the modes of vibrations, particularly in the 1500–1100 cm<sup>-1</sup> region. A  $\delta C_5 H$  mode hybridized with an in-phase combination of  $\nu N_1C_5$  and  $\nu N_3C_2$  gives a strong band at 1243 cm<sup>-1</sup> and an out-of-phase combination of  $\nu N_1 C_2$  and  $\nu N_1 C_5$  coupled with  $\nu N_3 C_2$  produces the strongest Raman band at 1215 cm<sup>-1</sup>. It is interesting to note that two strong bands are commonly observed in the 1260-1210 cm<sup>-1</sup> region of the Raman spectra excited with visible light, in spite of the large changes in vibrational mode associated with C<sub>2</sub>-deuteration. In the  $\pi \rightarrow \pi^*$  resonance Raman spectrum excited at 240 nm [8], the corresponding two bands are equally enhanced for 4-MeIm<sup>-</sup>- $d_0$ . However, only the low-frequency component is enhanced for 4-MeIm<sup>-</sup>-2- $d_1$  and the high-frequency component has no scattering intensity with 240 nm excitation. Since the modes that are resonance enhanced involve a symmetric stretch of the N<sub>1</sub>C<sub>2</sub>N<sub>3</sub> and/or an asymmetric stretch of the C<sub>2</sub>N<sub>1</sub>C<sub>5</sub>, it is very likely that the N<sub>1</sub>C<sub>2</sub> and  $N_3C_2$  bonds lengthen and the  $N_1C_5$  bond (possibly the  $N_3C_4$  bond also) shortens, or vice versa, upon  $\pi \rightarrow \pi^*$  excitation. The mode at ca 1530 cm<sup>-1</sup> is mainly contributed from  $\nu C_4 C_5$  and is also resonance enhanced with 240 nm excitation [8], indicating that the  $C_4 C_5$ bond also lengthens or shortens in the electronically excited state. It is highly probable that the imidazolate ring distorts upon  $\pi \rightarrow \pi^*$  transition in such a way that the bond length changes alternately in the  $C_4$ - $C_5$ - $N_1$ - $C_2$  and  $C_5$ - $C_4$ - $N_3$ - $C_2$  linkages in keeping the

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effective  $C_{2v}$  symmetry of the ring. Very recently, an *ab initio* calculation has shown that the  $C_4$ - $C_5$ ,  $N_1$ - $C_2$ , and  $N_3$ - $C_2$  bonds lengthen, and the  $N_1$ - $C_5$  and  $N_3$ - $C_4$  bonds shorten in a  $\pi$ - $\pi^*$  excited state of ImH<sub>2</sub><sup>+</sup> [22]. Analogous structural changes may also occur for Im<sup>-</sup>.

# CONCLUSION

Assignment of IR and Raman bands has been made for six isotopomers of Im<sup>-</sup> and four isotopomers of 4-MeIm<sup>-</sup>. The fundamental frequencies selected from the spectral data are consistently reproduced by normal coordinate calculations. The assignments and calculated normal modes help us to understand the vibrational properties of the imidazolate ring and to analyze the Raman bands of histidine residues in proteins. Analysis of the UV resonance Raman data based on the present normal coordinate calculations has suggested that the  $\pi \rightarrow \pi^*$  transition around 240 nm causes a symmetrical distortion of the imidazolate ring with alternating signs in bond length change.

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