

## The Vibrational Spectra of Succinimide and *N*-Deuteriosuccinimide

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The infrared spectra (4000–200 cm<sup>-1</sup>) of succinimide as a vapour (160 °C), melt (~130 °C), oriented polycrystalline film, KI-pellet, Nujol mull and dissolved in CCl<sub>4</sub>, CS<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>CN were recorded. Additional spectra were obtained in the region 400–30 cm<sup>-1</sup>. Raman spectra of the crystalline solid and saturated solutions in various polar solvents were recorded and semiquantitative polarization ratios were measured. Infrared and Raman spectra of *N*-deuteriosuccinimide in the solid state were recorded.

The fundamental frequencies were tentatively assigned in terms of *C*<sub>2v</sub> symmetry based upon Raman polarization data, dichroism of the oriented film and analogies with the spectra of the *N*-halogenated succinimides. Force fields were derived by initially transferring force constants from maleimide and succinic anhydride, and the data were fitted together with those of the *N*-halogenated succinimides by a least square method.

We have recently reported the vibrational spectra of maleic anhydride,<sup>1</sup> maleimide,<sup>2</sup> and *N*-chloromaleimide.<sup>3</sup> These studies have now been extended to the corresponding saturated cyclic imides. In the present communication we shall report our results for succinimide (SIM) and the *N*-deuterated species (SIMD), while the *N*-halogenated derivatives will be treated in a forthcoming paper.<sup>3</sup> Previously, infrared studies of SIM and SIMD as solids have been restricted to the KBr region<sup>5</sup> and oriented crystals in the NaCl region.<sup>6</sup> No melt or solution data have been reported and the Raman spectra have to our knowledge not been recorded.

In the present study we have obtained as complete infrared and Raman data as possible within the limitations imposed by the low vapour pressure and restricted solubility of

SIM. The assigned fundamentals were compared with the results of a normal coordinate analysis, using a generalized valence force field, and treating SIM and SIMD together with the *N*-halogenated succinimides.<sup>4</sup>

### EXPERIMENTAL

The sample of SIM was a commercial product from Fluka AG, which was purified by repeated sublimation on a cold finger (m.p. 126 °C, b.p. 287 °C). The deuterated compound (SIMD) was prepared by successive treatments with D<sub>2</sub>O and evaporation of the water. Although most of the sample handling took place in a dry box, a slight exchange of deuterium from moist air was observed in the infrared spectra.

The infrared, far infrared, and Raman (using the 4880 and 5145 Å lines from an argon ion laser (CRL 52 G)) spectrometers,<sup>1</sup> cells, and general procedures<sup>2</sup> have been described.

Dimethylformamide (DMFA) was used as solvent for the Raman spectra because of the low solubility of SIM in non-polar solvents.

### RESULTS

SIM and certain *N*-halogenated succinimides have been studied by X-ray crystallography and the ring skeleton reported<sup>7,8</sup> to be nearly planar. Furthermore, the same holds true for the related succinic anhydride in the vapour phase.<sup>9</sup>

The fact that SIM forms dimeric molecules in the crystal and probably in solution because of two N–H...O=C hydrogen bonds (contrary to the *N*-halogenated derivatives) presumably do not perturb the fundamentals significantly. As previously noted for the maleimides<sup>2,3</sup> the comparatively weak intermolecular bonds result in coinciding *a*<sub>g</sub> and *b*<sub>u</sub> as well as *a*<sub>u</sub>

and  $b_g$  modes ( $C_{2h}$  symmetry of the dimer). Only the N-H stretching and bending modes are highly affected by the hydrogen bonding. Therefore it seems appropriate to assume that SIM and SIMD (like the corresponding maleimide<sup>2</sup> and maleic anhydride<sup>1</sup>) have  $C_{2v}$  symmetry in all the states of aggregation. The 30 fundamentals will then divide themselves into the symmetry species:  $10a_1 + 5a_2 + 6b_1 + 9b_2$  in which  $a_1$  and  $b_2$  represent in-plane,  $a_2$  and  $b_1$  out-of-plane modes. All the fundamentals are active in the Raman effect while those of species  $a_2$  are forbidden in the infrared spectra.

A vapour IR spectrum of SIM was recorded at ca. 160 °C, but due to the low vapour pressure, the vapour contours gave no relevant information for the assignments. Instead, infrared measurements of the dichroic ratio of oriented polycrystalline films gave in many cases direct information about the species. This method, particularly suitable for orthorhombic crystals, has previously been applied to succinimide by Hayashii<sup>6</sup> and will therefore not be described here. Our dichroic measurements of various oriented polycrystalline films of SIM were much more complete in terms of spectral resolution and frequency range than the earlier work<sup>6</sup> employing NaCl-optics, but confirmed the earlier results.

Under the assumption of  $C_{2v}$  symmetry for the molecules, the transition moments will be directed along the X-, Y- and Z-axes (Fig. 2) for the  $b_1$ ,  $b_2$  and  $a_1$  modes, respectively. If an oriented gas model can be applied, the dichroic ratio should be equal for all vibrations belonging to the same species. In accordance with Hayashii's<sup>6</sup> determination of the crystal axes, the following infrared intensity ratios should be expected for SIM:

$$(a) I_b > I_c > I_a \text{ for } a_1$$

$$(b) I_c > I_a > I_b \text{ for } b_2$$

$$(c) I_a > (I_b \text{ and } I_c) \text{ for } a_1 \text{ vibrations.}$$

$I_a$ ,  $I_b$  and  $I_c$  denote the relative intensities for the three mutually perpendicular axes  $a$ ,  $b$  and  $c$  of the orthorhombic unit cell.

Additional support for the assignments was provided by the Raman polarization data obtained in saturated solutions in dimethylformamide and water. Also, the force constant

calculations of SIM and SIMD were of considerable aid. Moreover, the striking similarity between the spectra of SIM and those of *N*-chloro-, *N*-bromo-, and *N*-iodosuccinimide<sup>4</sup> was of great help for the assignments.

*Spectral interpretations.* As an illustration, the infrared spectra of two oriented polycrystalline films of SIM are shown in Figs. 1A ( $E$  vector parallel with the  $c$  and  $a$  axes) and 1B ( $E$  vector parallel with the  $b$  and  $a$  axes). The Raman spectrum of the solid is given in Fig. 1C, while the observed infrared and Raman frequencies are listed in Tables 1 (SIM) and 2 (SIMD). Our assigned fundamentals for both compounds are given in Table 3 together with the calculated frequencies.

The broad, intense bands at 3150 (solid), 3270 (melt) and 3280  $\text{cm}^{-1}$  ( $\text{CH}_3\text{CN}$  solution) were interpreted as the hydrogen bonded N-H stretch ( $\nu_1$ ). In  $\text{CCl}_4$  solution an infrared band at 3423  $\text{cm}^{-1}$  was considered as the "free"  $\nu_1$  (Table 1.) An intense infrared band at 3070  $\text{cm}^{-1}$  (solid) (absent for SIMD) disappeared in dilute solution and was assigned<sup>6</sup> as  $\nu_{23} + \nu_{24}$  in Fermi resonance with  $\nu_1$ . In SIMD the hydrogen bonded  $\nu_1$  was found at 2326  $\text{cm}^{-1}$  in the solid. The present data suggest that the hydrogen bonding is stronger in SIM than in maleimide since the N-H frequency shifts from dilute solution to melt and further to the solid state were larger for SIM. The two  $\text{CH}_2$  groups of SIM and SIMD will give rise to four C-H stretching frequencies (one of each species) which were attributed to bands between 3000 and 2940  $\text{cm}^{-1}$  in SIM, SIMD and the *N*-halogenated succinimides.<sup>4</sup>

It is well known from the maleimides,<sup>2,3</sup> maleic,<sup>1,10</sup> and succinic anhydride<sup>10</sup> that the C=O stretch of species  $a_1$  is invariably at higher frequency than the  $b_2$  mode. The same rule applies to SIM, SIMD and the *N*-halogenated succinimides and will be discussed in the forthcoming paper.<sup>4</sup> In SIM  $\nu_3$  and  $\nu_{23}$  were found at 1772 and 1697  $\text{cm}^{-1}$ , whereas in SIMD they were situated at 1771 and 1674  $\text{cm}^{-1}$ , respectively. A strong Raman band at 1766  $\text{cm}^{-1}$  in SIMD was interpreted as  $\nu_2 + \nu_{10}$  in Fermi resonance with  $\nu_3$ . The present molecules as well as the corresponding maleimides<sup>2,3</sup> and anhydrides<sup>1,10</sup> have several strong or medium intense bands in the region assigned

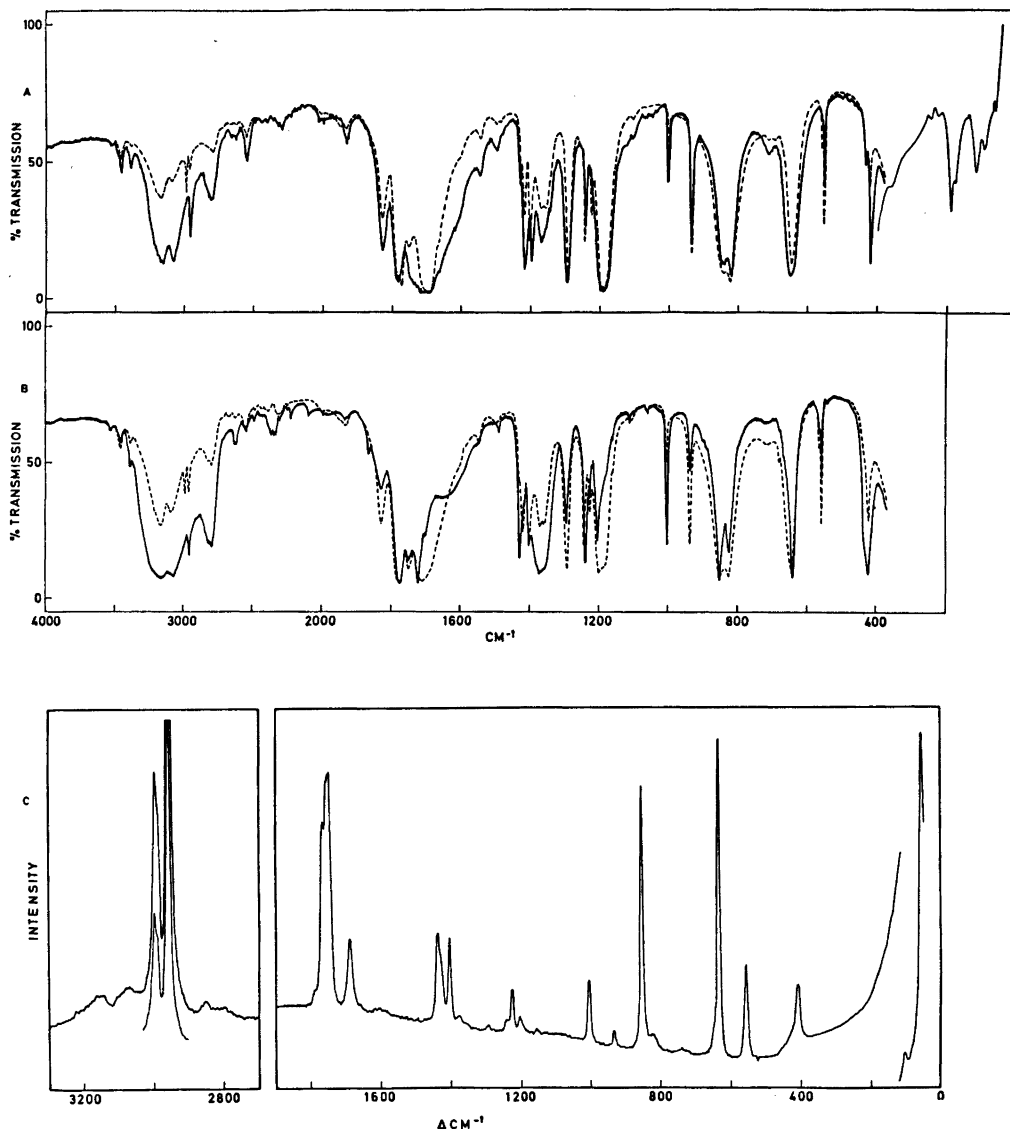


Fig. 1. Infrared and Raman spectra of succinimide in the solid state: A. (upper curve) 4000–400  $\text{cm}^{-1}$ : the infrared spectrum of oriented crystals between KBr plates; solid line,  $E$  vector along  $c$  axis; dotted line,  $E$  vector along  $a$  axis. 400–30  $\text{cm}^{-1}$ : polyethylene pellet; B. (middle curve) the infrared spectrum of oriented crystals between KBr plates; solid line,  $E$  vector along  $b$  axis; dotted line,  $E$  vector along  $a$  axis; C. (lower curve) the Raman spectrum.

to combination bands or overtones, partly enhanced by Fermi resonance to the  $a_1$  and  $b_2$  fundamentals.

The two methylene groups of SIM and SIMD will give rise to two scissor ( $a_1, b_1$ ), wag ( $a_1, b_2$ ), twist ( $a_2, b_1$ ) and rock ( $a_2, b_1$ ) fundamentals

of which the scissor and wag are generally localized vibrations situated around 1450 and 1300  $\text{cm}^{-1}$ , respectively. All the succinimides<sup>4</sup> had intense infrared and Raman bands around 1425  $\text{cm}^{-1}$  assigned to an  $a_1$  mode. The corresponding  $b_2$  scissoring modes ( $\nu_{25}$ ) were assigned

Table 1. Infrared and Raman spectral data for succinimide.

Infrared <sup>a</sup>			Melt		Raman		Assignments <sup>b</sup>
Solid	Oriented crystals		~ 130 °C		Solid	Solution	
Nujol	$\alpha$ -axis	$b$ -axis	$c$ -axis			DMFA <sup>d</sup>	
3447 w <sup>c</sup>	3451 w	3451 w l	3449 w i				$\nu_3 + \nu_{23} = 3469 B_2$
3375 w	3374 vw l	3378 w	3375 w				$\nu_1$ free $a_1$
3150 s	3155 s l	3155 s i	3150 s	3270 s			$2 \times \nu_{23} = 3394 A_1$
3070 s /	3075 s l	3075 s i	3075 s	3075 m sh	3070 vw	3081 w	$\nu_1$ H bonded $a_1$
						3000 s	$\nu_{23} + \nu_{24} = 3113 A_1, FR$
						2990 sh	$\nu_{11}$ fund. $a_2$
						2960 vs	$\nu_{16}$ fund. $b_1$
							$\nu_2$ fund. $a_1$
2946 m /	2951 w	2954 w l	2949 m	2944 w			$\nu_{22}$ fund. $b_2$
	2920 vw sh		2918 vw i				$\nu_7 + \nu_{23} = 2935 B_2$
			2820 w sh l				$2 \times \nu_{24} = 2832 A_1$
2536 w	2788 m l	2815 m i	2795 m	2740 w	2800 w	2825 sh <sup>g</sup>	$\nu_4 + \nu_5 = 2801 A_1$
2000 vw	2540 w	2640 w l	2532 m	2510 w	2527 w		$\nu_5 + \nu_{27} = 2565 B_2$
1930 w	2012 vw		2015 w i	1980 vw			$\nu_5 + \nu_{28} = 2023 B_2$
1860 w	1830 w	1830 vw	1927 w i	1912 vw			$\nu_7 + \nu_{28} = 1936 B_2$
1827 m	1826 m	1862 w sh i	1860 w sh	1800 sh	1865 w	1820 w P	$2 + \nu_{28} = 1870 A_1$
1781 sh	1782 s sh	1826 m l	1826 s	1800 w	1790 sh		$\nu_9 + \nu_{27} = 1832 B_2, FR$
1772 s	1770 s	1773 s l	1782 s i	1775 s	1768 s } 1746 s }	1776 s P	$\nu_8 + \nu_{28} = 1785 B_2, FR$
1747 sh	1745 m	1746 m l	1740 s sh				$\nu_3$ fund $a_1$
1697 vs	1700 s	1700 m sh	1700 s i		1690 m	1710 w D <sup>g</sup>	$\nu_{15} + \nu_{30} = 1780 B_1$
							$\nu_{23}$ fund. $b_2$
	1682 sh	1721 m	1682 sh	1710 sh			$\nu_{17} + \nu_{20} = 1743 A_1$
	1665 sh	1650 sh	1600 sh				$\nu_8 + \nu_{18} = 1694 B_1$
1600 vw sh	1600 sh	1545 w sh l	1542 w i		1665 sh		$2 \times \nu_{18} = 1688 A_1$
1545 w	1495 vw	1495 vw	1497 w	1560 w bd			$\nu_{10} + \nu_{27} = 1619 B_2$
	1487 vw l	1487 vw i	1485 vw sh				$\nu_7 + \nu_{30} = 1557 B_2$
1428 s	1429 w	1428 s	1427 w	1429 s	1438 m	1432 s P <sup>g</sup>	$\nu_8 + \nu_9 = 1500 B_2$
1416 m	1417 m	1417 sh l	1415 s		1428 sh	1417 s D	$\nu_4$ fund. $a_1$
1402 m sh } 1396 m }	1402 m	1402 m	1395 s	1390 m sh	1402 m		$\nu_{24}$ fund. $b_1$
				1390 s sh <sup>h</sup>			$\nu_{25}$ fund. $b_2$

Table 1. Continued.

1373 s <sup>h</sup>	1369 m	1370 s i	1368 s	1345 s	1337 s	1376 w	1380 w P <sup>g</sup>	$\nu_6$ fund. $a_1$
1355 sh <sup>f</sup>	1355 m sh	1355 sh l	1355 sh l	1291 s	1287 s <sup>h</sup>	1294 w	1301 vw <sup>g</sup>	$\nu_{17} + \nu_{21} = 1370 A_1$
1294 s	1290 s	1293 s l	1292 s i	1238 s	1282 w <sup>i</sup>			$\nu_{26}$ fund. $b_2$
				1225 w sh	1240 s <sup>h</sup>	1240 sh	1240 sh P	$2 \times \nu_{29} = 1300 A_1$
1238 s	1242 s l	1238 s i	1242 s	1170 s	1226 w <sup>i</sup>	1227 m	1228 m D	$\nu_6$ fund. $a_1$
1224 w	1223 w i	1225 w	1192 s i	1105 w	1164 s <sup>i</sup>	1205 w	1159 w D <sup>g</sup>	$\nu_{12}$ fund. $a_2$
1192 s	1195 s	1200 sh l	1180 s i	999 m	1175 sh <sup>i</sup>		1180 vw D	$\nu_{27}$ fund. $b_2$
1180 s	1180 s l	1180 s l	1180 s i	913 s	1115 w <sup>i</sup>			$\nu_{17}$ fund. $b_1$
1109 vw	1105 w l	1109 w	1105 w	850 s	999 m <sup>h</sup>	1005 m	1005 s P	$\nu_{13} + \nu_{21} = 1125 B_2$
1001 m	1000 m l	1001 s	1003 m	840 s				$\nu_7$ fund. $a_1$
993 sh				818 s				$\nu_{10} + \nu_{20} = 990 B_1$
935 s	935 s	935 m	936 s i	760 w bd	787 s <sup>i</sup>	822 w	825 w sh D	$\nu_{28}/\nu_{13}$ fund. $b_2$
850 s	850 s	850 s i	850 s	676 vw	765 w sh <sup>i</sup>	739 w	717 vw	$\nu_8$ fund. $a_1$
844 sh	840 s sh	840 s	840 s	633 s		725 w sh		$\nu_{18}$ fund. $b_1$
823 s	822 s	823 s l	821 s	565 vw				$\nu_{19}$ fund. $b_1$
				545 s				$\nu_{21} + \nu_{21} = 830 B_1$
								$\nu_{21} + \nu_{30} = 746 A_2$
								$\nu_{14} + \nu_{21} = 727 B_2$
720 w <sup>f</sup>	715 vw	715 vw l	715 vw i	676 vw	668 w <sup>h</sup>	650 sh	630 s P	$\nu_{12} - \nu_{30} = 667 B_1$
669 vw sh	678 w i	678 w l	678 w	633 s		635 s	564 sh D <sup>g</sup>	$\nu_{29}$ fund. $b_2$
650 s	644 s	644 s l	650 s i	562 vw	632 s <sup>h</sup>	563 sh	547 s D	$\nu_9$ fund. $a_1$
640 s	644 s l	640 s i	638 s	545 s	550 sh <sup>h</sup>	555 m		$\nu_{30}$ fund. $b_1$
563 w sh	563 w i	562 w	562 vw		545 m <sup>h</sup>	530 w		$\nu_{30}$ fund. $b_2$
556 m	556 s	556 m l	555 m					$\nu_{14}$ fund. $a_2$
537 vw	538 vw	538 vw i	538 vw		415 m sh <sup>h</sup>	408 m	415 w <sup>g</sup>	$\nu_{15} + \nu_{21} = 455 B_2$
	434 w l	434 m sh i	434 w		400 s	267 w	360 vw bd <sup>g</sup>	$\nu_{10}$ fund. $a_1$
427 s	420 s l	418 s i	419 s		360 w <sup>h</sup>			$2 \times \nu_{21} = 380 A_1$
360 m <sup>f</sup>					160 s <sup>h</sup>			$\nu_{15}$ fund. $a_2$
190 s								$\nu_{21}$ fund. $b_1$
177 m								lattice modes
146 vw						105 m		

<sup>a</sup> The weak infrared and Raman bands in the regions 5000–3500 and 2900–2000 cm<sup>-1</sup> are omitted.

<sup>b</sup> When available the combination frequencies and overtones are calculated from infrared solid data.

<sup>c</sup> w, weak; m, medium; s, strong; v, very; bd, broad; sh, shoulder; P, polarized and D, depolarized; Fr, Fermi resonance, i and l denote intensified and lowered absorptions with polarized radiation.

<sup>d</sup> Dimethylformamide. <sup>e</sup> CH<sub>3</sub>CN solution. <sup>f</sup> KBr pellet. <sup>g</sup> H<sub>2</sub>O solution. <sup>h</sup> CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>i</sup> CS<sub>2</sub> solution. <sup>j</sup> Solid state frequencies below 200 cm<sup>-1</sup> are from polyethylene (Rigidex pellet). <sup>k</sup> C<sub>6</sub>H<sub>6</sub> solution.

Table 2. Infrared and Raman spectral data for *N*-deuteriosuccinimide.

IR Solid Nujol	Raman Solid	Assignments <sup>b</sup>	IR Solid Nujol	Raman Solid	Assignments <sup>b</sup>		
3146 m <sup>c</sup>		H <sup>d</sup>		1213 vw	$\nu_{10} + \nu_{24} = 1239$ $\bar{H}/\nu_{17}$ fund.	$B_2$ $b_1$	
3060 m		H	1190 s	1150 vw	$\nu_{9/25} + \nu_{10} = 1160$	$B_1/A_2$	
	2998 s	$\nu_{11}$ fund.		1115 w	$2 \times \nu_{20} = 1126$	$A_1$	
	2989 s	$\nu_{16}$ fund.		1101 w sh	$\nu_{13} + \nu_{21} = 1103$	$B_2$	
	2958 vs	$\nu_3/\nu_{23}$ fund.		1096 s	$\nu_{28}$ fund.	$b_2$	
2398 s sh	2400 vw	$\nu_4 + \nu_7 = 2424$		1060 w	$2 \times \nu_{14} = 1080$	$A_1$	
2386 s		$\nu_{28} + \nu_{28} = 2388$		1045 w sh	$\nu_{10} + \nu_{20} = 1054$	$B_2$	
	2331 m sh			1002 w sh	H		
2326 s	2317 m	$\nu_1$ fund.		999 m	$\nu_7$ fund.	$a_1$	
	2284 w sh	$\nu_7 + \nu_{26} = 2291$		973 vw	$\nu_{10} + \nu_{20} = 982$	$B_1$	
2245 w sh	2245 vw	$\nu_7 + \nu_{27} = 2271$		932 w	H		
2205 m		$\nu_6 + \nu_7 = 2230$		916 vw	$\nu_{13}$ fund.	$a_2$	
2180 sh		$\nu_3 + \nu_{10} = 2190$		890 vw	$\nu_{15} + \nu_{25} = 903$	$B_1$	
1900 vw		$\nu_5 + \nu_{20} = 1906$		846 s	$\nu_8/\nu_{18}$ fund.	$a_1/b_1$	
1822 w		$\nu_{28} + \nu_{30} = 1840$		832 sh	$2 \times \nu_{10} = 838$	$A_1$	
	1766 s	$\nu_5 + \nu_{10} = 1777$		820 s	$\nu_{24}$ fund.	$b_2$	
1771 s	1752 s	$\nu_3$ fund.		754 w	$\nu_{15} + \nu_{15} = 793$	$B_2$	
	1743 s sh			635 s	$\nu_9/\nu_{29}$ fund.	$a_1/b_2$	
1695 s		H		589 vw	$\nu_{10} + \nu_{21} = 606$	$B_1$	
1674 s	1667 m	$\nu_{23}$ fund.		564 w	$\nu_{20}$ fund.	$b_1$	
1655 sh		$\nu_{15} + \nu_{25} = 1670$		563 w	H		
1522 vw sh		$\nu_{15} + \nu_{27} = 1540$		556 w			
	1468 w	$\nu_8 + \nu_7 = 1480$		548 m	548 s	$\nu_{30}$ fund.	$b_2$
1425 m	1428 m	$\nu_4$ fund.		525 m	543 w sh	$\nu_{14}$ fund.	$a_2$
1402 w	1406 m	$\nu_{25}$ fund.		419 s	480 w bd	$\nu_{19}$ fund.	$b_1$
1395 vw sh		$\nu_8 + \nu_{20} = 1409$		360 w bd <sup>e</sup>	418 s	$\nu_{10}$ fund.	$a_1$
1358 s	1359 w	$\nu_5$ fund.			268 vw	$2 \times \nu_{21} = 374$	$A_1$
1335 w sh		$\nu_{17} + \nu_{21} = 1367$				$\nu_{15}$ fund.	$a_2$
1292 s		$\nu_{28}$ fund.		187 s		$\nu_{21}$ fund.	$b_1$
1272 s	1281 vw	$\nu_{27}$ fund.		176 s			
1265 s sh		$2 \times \nu_{20} = 1270$		130 m			
1247 w	1241 vw sh	$\nu_8 + \nu_{10} = 1265$			125 w		} lattice modes
1231 m	1228 m	$\nu_6$ fund.			105 w		
1222 w sh		$\nu_{13}$ fund.		91 m			

<sup>a</sup> The weak infrared and Raman bands in the regions 5000–3200 and 2800–2500  $\text{cm}^{-1}$  are omitted. <sup>b</sup> When available the combination frequencies and overtones are calculated from solid state data. <sup>c</sup> For abbreviations used, see footnotes to Table 1. <sup>d</sup> H = bands assigned to succinimide. <sup>e</sup> Solid state frequencies below 400  $\text{cm}^{-1}$  are from polyethylene (Rigidex) pellet.

to bands around 1400  $\text{cm}^{-1}$  in accordance with the observed dichroism. Correspondingly, the wagging fundamentals  $\nu_8$  and  $\nu_{28}$  were observed at 1238 and 1294  $\text{cm}^{-1}$  (SIM) and 1231 and 1292  $\text{cm}^{-1}$  (SIMD).

The 1373  $\text{cm}^{-1}$  band which was clearly of species  $a_1$  involves predominantly CNC stretch, close to the corresponding frequencies for the maleimides.<sup>2,3</sup> An infrared band at 1416 (SIM) and 820  $\text{cm}^{-1}$  (SIMD) was interpreted as the N–H(D) in-plane bend. In agreement with the observed dichroism and Raman polarization data, the 1225  $\text{cm}^{-1}$  band (SIM) is taken as the

$\text{CH}_2$  twist of species  $a_2$  ( $\nu_{12}$ ). The corresponding  $b_1$  mode ( $\nu_{17}$ ) is assigned to the band at 1180  $\text{cm}^{-1}$  partly overlapping the  $b_2$  fundamental ( $\nu_{27}$ ), which involves the CNC stretch. Similar bands are found for SIMD at 1222, 1190 and 1272  $\text{cm}^{-1}$ , respectively.

Three skeletal modes ( $\nu_7$ ,  $\nu_{28}$ ,  $\nu_8$ ) with strong contributions from skeletal C–C stretch are found at 1001, 935 and 850  $\text{cm}^{-1}$  for SIM and at 999, 1096 and 846  $\text{cm}^{-1}$  for SIMD. For SIMD as well as for *N*-deuteriomaleimide<sup>2</sup> the  $b_2$  modes of the region 1300–800  $\text{cm}^{-1}$ , not localized to the methylene groups, are highly

Table 3. Observed ( $\nu_o$ ) and calculated ( $\nu_c$ ) fundamentals for succinimide and *N*-deuteriosuccinimide.

Species and No.	Succinimide		<i>N</i> -Deuteriosuccinimide		
	$\nu_o^a$	$\nu_c$	$\nu_o^a$	$\nu_c$	
$a_1$	$\nu_1$	3150	3151	2326	
	$\nu_2$	2960	2946	2958	
	$\nu_3$	1772	1773	1771	
	$\nu_4$	1428	1412	1425	
	$\nu_5$	1373	1403	1358	
	$\nu_6$	1238	1239	1231	
	$\nu_7$	1001	973	999	
	$\nu_8$	850	839	846	
	$\nu_9$	640	640	635	
	$\nu_{10}$	427	414	419	
$a_2$	$\nu_{11}$	3000	2998	2998	
	$\nu_{12}$	1224	1190	1222	
	$\nu_{13}$	935	1064	916	
	$\nu_{14}$	537	538	543	
	$\nu_{15}$	267	292	268	
$b_1$	$\nu_{16}$	2990	2988	2989	
	$\nu_{17}$	1180	1197	1190	
	$\nu_{18}$	844	749	846	
	$\nu_{19}$	823	860	525	
	$\nu_{20}$	563	536	563	
	$\nu_{21}$	190	184	187	
	$b_2$	$\nu_{22}$	2946	2946	—
		$\nu_{23}$	1697	1698	1674
		$\nu_{24}$	1416	1427	820
		$\nu_{25}$	1402	1403	1402
$\nu_{26}$		1294	1310	1292	
$\nu_{27}$		1192	1173	1272	
$\nu_{28}$		935	941	1096	
$\nu_{29}$		650	666	635	
$\nu_{30}$		556	553	548	

<sup>a</sup> When possible, frequencies are taken from the infrared spectra of the solids.

mixed compared to the parent molecules, and therefore causing erratic isotopic shifts.

The  $\text{CH}_2$  rock of species  $a_2$  ( $\nu_{13}$ ) was found between 935 and 908  $\text{cm}^{-1}$  for SIMD and the *N*-halogenated succinimides.<sup>4</sup> For SIM this fundamental presumably overlaps the more intense  $b_2$  mode at 935  $\text{cm}^{-1}$ .

For SIM three overlapping bands are situated between 850 and 820  $\text{cm}^{-1}$ . From comparison with the *N*-halogenated succinimides<sup>4</sup> the bands at 844  $\text{cm}^{-1}$  are considered as the  $\text{CH}_2$  rock ( $\nu_{18}$ ) of species  $b_1$ , while the stronger lines at 823  $\text{cm}^{-1}$  are attributed to the *N*-H out-of-plane bend ( $\nu_{19}$ ). For SIMD the  $\text{CH}_2$  rock of species  $b_1$  overlaps the  $a_1$  fundamental  $\nu_8$  at 846  $\text{cm}^{-1}$ . The *N*-D bending mode of species  $b_1$ , is situated at 525  $\text{cm}^{-1}$  and corresponds

to the band at 518  $\text{cm}^{-1}$  for *N*-deuteriomaleimide.<sup>2</sup>

In complete agreement with the results for the maleimides<sup>2,3</sup> the succinimides have two bands in the region 640–680  $\text{cm}^{-1}$  taken as  $\nu_9$  ( $a_1$ ) and  $\nu_{20}$  ( $b_2$ ), the former being more intense in the Raman spectrum.

Weak bands at 537 and 543  $\text{cm}^{-1}$  for SIM and SIMD, respectively, are attributed to a skeletal mode ( $\nu_{14}$ ) of species  $a_2$  while the corresponding  $b_1$  fundamental ( $\nu_{20}$ ) is assigned to the band 563  $\text{cm}^{-1}$  for both molecules.

For SIM the 563  $\text{cm}^{-1}$  band presumably overlaps a fundamental ( $\nu_{30}$ ) of species  $b_2$ , mainly involving the asymmetrical bending of the C=O groups. The corresponding  $a_1$  mode ( $\nu_{16}$ ) is assigned to the strong infrared and Raman bands at 427  $\text{cm}^{-1}$  in good agreement with the results from the maleimides.<sup>2</sup> Similar bands are found for SIMD at 548 and 419  $\text{cm}^{-1}$ , respectively.

The remaining two fundamentals  $\nu_{15}$  ( $a_2$ ) and  $\nu_{21}$  ( $b_1$ ) are attributed to the bands at 265 and 190  $\text{cm}^{-1}$  for SIM and at 268 and 187  $\text{cm}^{-1}$  for SIMD, in good agreement with the results for the maleimides.<sup>2,3</sup>

#### NORMAL COORDINATE ANALYSIS

Detailed knowledge about the harmonic force constants cannot be obtained for SIM and the *N*-halogenated succinimides<sup>4</sup> independently since the information from the normal vibrations is insufficient for this purpose. Also, the ambiguities in the assignments suggested us to use force constant calculations as a tool for obtaining more reliable assignments rather than determining force constants of general physical significance. Therefore, the scope of this section is to demonstrate that the approximation of transferable force constants may be applied in establishing reliable spectral interpretations of SIM, SIMD as well as the *N*-halogenated succinimides.<sup>4</sup>

The normal coordinate analysis was carried out employing an approximate internal valence force field (IVFF), and the least squares method was applied in adjusting the force constants. As a starting point we used the force fields for maleimide<sup>2</sup> and succinic anhydride.<sup>10</sup> The related structure and spectral similarities of all the succinimides (*N*-H, *N*-D, *N*-Cl,

Table 4. Final valence force constants for succinimide.

Force type	Constants	
	Symbol <sup>a</sup>	Value <sup>b</sup>
stretch	$K_a$	5.297
	$K_s$	11.611
	$K_r$	3.934
	$K_d$	3.5
	$K_l$	4.798
	$K_b$	5.456
stretch-stretch	$K_{a_1a_2}$	1.045
	$K_{a_1s_1}$	1.53
	$K_{a_1s_2}$	-0.04
	$K_{s_1s_2}$	0.3
	$K_{a_1r_1}$	1.087
	$K_{r_1d}$	0.211
	$K_{l_1l_2}$	-0.079
bend	$H_\eta$	1.185
	$H_\xi$	1.185
	$H_\psi$	0.574
	$H_\phi$	0.574
	$H_\theta$	0.538
	$H_\alpha$	1.344
	$H_\epsilon$	1.079
	$H_\beta$	1.566
	$H_\mu$	0.47
stretch-bend	$F_{a\eta}$	0.17
	$F_{r\xi}$	0.17
	$F_{s\alpha}$	-1.19
	$F_{r\psi}$	0.15
	$F_{d\phi}$	0.15
bend-bend	$F_{\psi_1\psi_2}$	-0.038
	$F_{\phi_1\phi_2}$	-0.038
	$F_{\psi_1\phi_1}$	-0.015
outo <sup>c</sup>	$O_{\pi_1}$	0.411
	$O_{\pi_2}$	0.363
outo-outo	$O_{\pi_1\pi_2}$	0.086
torsion	$T_\tau$	0.931
outo-torsion	$F_{\pi_1\tau_1}$	-0.118
	$F_{\pi_2\tau_1}$	0.173
torsion-torsion	$T_{\tau_1\tau_2}$	-0.031

<sup>a</sup> For meaning of symbols, see Fig. 2. <sup>b</sup> In units of mdyne Å<sup>-1</sup> (stretch constants), mdyne rad<sup>-1</sup> (stretch-bend interaction) and mdyne Å rad<sup>-2</sup> (bending and torsion constants). <sup>c</sup> outo means out-of-plane bending.

N-Br, N-I) justified the use of transferable force constants. We therefore employed data from all the five compounds simultaneously in the least squares fitting, keeping the force constants concerning the H<sub>2</sub>-C-C-H<sub>2</sub> part of the molecule at the same value for all.

Moreover, we decided to give the C=O bending force constants and some of the interaction constants a common value for all the compounds. To reduce the number of parameters further we have made  $H_\eta$  and  $H_\xi$ ,  $H_\psi$  and  $H_\phi$ ,  $F_{a\eta}$  and  $F_{r\xi}$ ,  $F_{r\psi}$  and  $F_{d\phi}$ ,  $F_{\psi_1\psi_2}$  and  $F_{\phi_1\phi_2}$  equal. The final force field consisted of 81 parameters. It was reported<sup>11</sup> that for similar molecules the C=O stretching frequencies can be calculated correctly by using interaction terms between the two C=O bonds, the two C-N bonds and between the C=O and C-N bonds. This model force field was also suitable for the succinimides. For the remaining interaction constants we have only introduced terms between neighbouring groups.

Since the most complete data were obtained for the solid state, we have employed these frequencies in the calculations leading to even more approximate force constants due to crystal effects. The agreement between observed

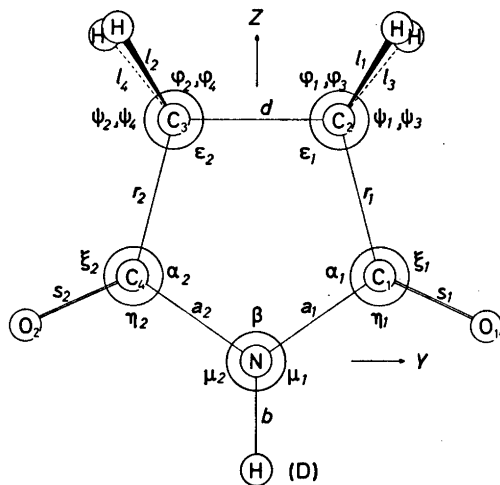


Fig. 2. Internal coordinates for succinimide. The following coordinates are not shown in the figure: out-of-plane bending:  $\pi_1 = \pi(\text{NC}_2\text{C}_1\text{O}_1)$ ,  $\pi_2 = \pi(\text{C}_3\text{NC}_4\text{O}_2)$ ,  $\pi_3 = \pi(\text{C}_4\text{C}_1\text{NH})$ ; torsion:  $\tau_1 = \tau(\text{NC}_1\text{C}_2\text{C}_3)$ ,  $\tau_2 = \tau(\text{NC}_4\text{C}_3\text{C}_2)$ . The out-of-plane bending and torsion coordinates are defined as in Wilson, Decius and Cross,<sup>12</sup> where the succession of the letters corresponds to atom 2, 3, 4, 1 in the definition of the out-of-plane bending coordinate.  $\theta_1, \theta_2$ : the bending of the angles HCH. The following structural parameters were assumed: CN: 1.379; C<sub>1</sub>-C<sub>2</sub>: 1.477; C<sub>2</sub>-C<sub>3</sub>: 1.520; C=O: 1.220; C-H: 1.09; N-H: 0.99 Å;  $\angle\text{CNC}$ : 110.0°;  $\angle\text{NCC}$ : 110.5°;  $\angle\text{NCO}$ : 122.9° and  $\angle\text{C}_1\text{C}_2\text{H}$ : 116.1°.



and calculated frequencies was quite good for the  $a_1$  and  $b_2$  species, while some large discrepancies still remained for the out-of-plane modes. This may very well be due to large amplitudes of certain out-of-plane vibrations as mentioned in Ref. 9. For the  $a_2$  and  $b_1$  fundamentals (except those involving the  $\text{CH}_2$  groups) we have employed an almost complete force field, using the approximation of keeping some of the interaction constants common for all the molecules. Since the assignments for these species are not as certain as for the in-plane modes and the force constants not as physically interesting, we do not consider it worth while to make any further calculations to achieve a better fit. Later, we will expand the calculations with more data from succinic anhydride and the  $C$ -deuterated species of both succinimide and succinic anhydride.

The internal in-plane coordinates are shown in Fig. 2, and the out-of-plane coordinates are given in the underlying text. Our calculated fundamentals are listed together with the observed frequencies in Table 3. The final set of force constants for SIM and SIMD are given in Table 4. The results seem physically reasonable, although the restrictions imposed, keeping some of the force constants transferable to the halogenated molecules and using as few constants as possible, are reflected in some of the values. The potential energy distribution (PED) of the fundamentals among the valence coordinates were calculated. These data were not included in Table 3 for the sake of brevity, but can be obtained from the authors on request.

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