SCALED QUANTUM MECHANICAL (SQM) AB INITIO FORCE FIELD AND VIBRATIONAL SPECTRA OF MALEIMIDE (1H-PYRROLE-2,5-DIONE)

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ABSTRACT

The vibrational spectrum of free maleimide has been interpreted using a theoretical general valence force field (GVFF) calculated ab initio at the Hartree—Fock level using the 4-21 split valence basis set. The directly computed GVFF was scaled with 14 empirical factors transferred from other molecules. The vibrational fundamentals predicted by this scaled GVFF enabled corrections to be suggested for several previous empirical assignments. The scale factors were also optimized directly on the experimental spectrum of maleimide producing the best GVFF obtainable from combined experimental and theoretical evidence. This scaled GVFF yielded frequencies agreeing with experimental values and with mean deviations of 6.8 and 9.6 cm^{-1} for in-plane and out-of-plane frequencies, respectively. The vibrational frequencies of the ^2H and ^{15}N isotopomers of C_{2v} symmetry are also presented and discussed.

INTRODUCTION

Ab initio calculations with a moderate sized basis set (double zeta or split valence) and with simple empirical corrections have been shown to be very effective both in structural studies and vibrational analyses. For reviews, see refs. 1—4; some more recent results are collected under refs. 5—8. The applications for the determinations of geometry parameters are reviewed by Schäfer [9] but it must be emphasized that this work refers to attempts to approximate r_0 geometries. The successful use of scaled quantum mechanical (SQM) force fields in vibrational analyses of larger molecules (e.g., pyridine [5], cyclohexane [6], γ-pyrone [7]), suggests the general applicability of the method to complex molecules which are practically untreatable by conventional normal coordinate analysis.

Simple heterocycles containing N and a peptide linkage are of essential importance for studies of biological systems. The five-membered ring of

maleimide (MM) is very well suited to serve as a model for both peptides or proteins and pyrimidine bases. Its gas phase molecular structure has been recently determined [10, 11]. On the other hand, its vibrational spectrum has been extensively studied by both infrared and Raman techniques in various phases, including gas, solution (in a number of solvents), melt and solid [12—24]. These studies also provide information on the vibrational frequencies of some deuterated and ^{15}N substituted species which can be valuable in the assignment of particular normal modes. In spite of considerable experimental efforts, certain contradictions can be observed among the available data, as was shown by Harsányi et al. [25] for a CNDO/2 force field study.

In the present work, we give a summary of the computational details, the geometry, the force constants and the vibrational frequencies and intensities of the absorption bands of MIM and its C_{2v} symmetry isotopomers obtained from ab initio calculations. These data, and the accuracy and reliability of vibrational analyses at the semi-empirical level are then compared with those from ab initio studies.

COMPUTATIONAL DETAILS

In the computation of the force constants of MIM, the standardized procedure previously recommended by our group [26, 27] was followed. The program TEXAS [28] with the split valence 4-21 basis [26] was used throughout unless otherwise specified.

The theoretical equilibrium geometry belonging to the global minimum of the energy hypersurface was calculated using the GDIIS algorithm [29]. In order to obtain the best estimate of the true equlibrium geometry, as needed for the reference geometry in the force field calculations, the small empirical corrections of ref. 26 were applied to the theoretical bond distances.

In a separate calculation the geometry was also optimized using an extended basis set (4-21N*), i.e., with d-type polarization functions (exponent 0.8) placed on the nitrogen atom only. This study was suggested by results on 4-pyridone [30—32] which raised doubts about the planarity of nitrogen-containing rings. In addition, some force constants were also calculated with the same extended basis set. As discussed below, both the geometry and out-of-plane force constants corroborated the planarity of the molecule.

The force constants were obtained by numerical differentiation of the gradients obtained from calculations at distorted positions, both in the positive and negative senses, around the reference geometry. Distortions were made along the internal coordinates shown in Table 1. The actual displacements were ±2 pm for stretching, ±0.02 rad for in-plane bending and ±0.10 rad for out-of-plane bending and torsional coordinates.

The theoretical force constants were scaled to fit experimental frequencies using a small set of scale factors as described in ref. 27. A set of previously recommended values of the scale factors [27] was first applied to check the

TABLE 1

Definition of internal coordinates of maleimide

No.	Description	Symbols	Definition[a]
1	NH stretching	ν_{NH}	r_1
2, 3	CH stretching	ν_{CH}	r_2, r_3
4, 5	C=O stretching	$\nu_{C=O}$	r_4, r_5
6, 7	NC stretching	ν_{NC}	R_1, R_2
8, 9	CC stretching	ν_{CC}	R_3, R_4
10	C=C stretching	$\nu_{C=C}$	R_5
11	NH bending	β_1	$\beta_{12} - \beta_{15}$
12, 13	CH bending	β_2, β_3	$\beta_{32} - \beta_{34}; \beta_{45} - \beta_{43}$
14, 15	C=O bending	β_4, β_5	$\beta_{21} - \beta_{23}; \beta_{51} - \beta_{54}$
16, 17[b]	ring deformation	α_1	$\alpha_1 + a(\alpha_2 + \alpha_5) + b(\alpha_3 + \alpha_4)$
		α_2	$(a - b)(\alpha_2 - \alpha_5) - (1 - a)(\alpha_3 - \alpha_4)$
18	NH out-of-plane bending	γ_1	γ_1
19, 20	CH out-of-plane bending	γ_2, γ_3	γ_2, γ_3
21, 22	C=O out-of-plane bending	γ_4, γ_5	γ_4, γ_5
23, 24[b]	ring torsion	τ_1	$b(\tau_{5123} + \tau_{2154}) + \tau_{2345} + a(\tau_{1234} + \tau_{1543})$
		τ_2	$(a - b)(\tau_{1234} - \tau_{1543}) + (1 - a)(\tau_{2154} - \tau_{5123})$

[a] In-plane symbols used are shown in Fig. 1. The index of the out-of-plane bending coordinates corresponds to the numbering of the atoms in Fig. 1, γ_i is positive if atom i moves in the positive z direction. The four indices in the torsion are also numbers of the atoms (i.e., τ_{2345} is the dihedral angle of the 234 and 345 planes). The torsional angle τ_{ijkl} is positive if, viewing from the direction of atom k, an anti-clockwise rotation is needed to bring atoms i and l into eclipsed conformation. Normalization factors of composite coordinates are omitted. [b] $a = \cos 144°$, $b = \cos 72°$.

reliability of the assignment. Then, after changing the assignment in a few cases, the scale factors were optimized in the least-square sense. Altogether 14 scale factors of the same type as in the CNDO/2 study [25] were used in this second optimization.

The vibrational frequencies were calculated according to Wilson's GF-method [33]. For a better characterization of the predicted normal vibrations, absolute intensities of the infrared bands were also calculated from dipole moment derivatives with respect to internal coordinates, intensity values calculated at this quantum mechanical level are expected to agree semi-quantitatively with experimental observations [1—4].

The description of the normal modes is given in the terms of the M-matrix elements [34], for detailed reasoning see ref. 27.

RESULTS AND DISCUSSION

Geometry

The geometry parameters obtained using the 4-21 and 4-21N* bases are listed in Table 2. For a comparison, the calculated CNDO/2 [25], MNDO/3 [35] and experimentally obtained [11] bond distances and angles are also

TABLE 2

Theoretical and experimental geometries of maleimide (MIM)

Parameter[a]	Semiempirical		Ab initio			Exp.(ED)[g]
	r_e(CNDO)[b]	r_e(MINDO)[c]	r_e(4-21)[d]	r_e(4-21-N*)[e]	r_{ref}[f]	
Bond lengths						r_g
N_1—C_2	139.4	139.8	139.2	138.9	138.3	140.9(3)
C_2—C_3	145.5	150.8	150.9	150.6	150.0	150.8(3)
C_3=C_4	134.0	134.8	131.6	131.5	133.8	134.4(4)
N_1—H_8	106.1	102.4	99.4	99.4	99.9	102.5[h]
C_2=O_6	127.1	120.3	120.4	120.4	120.4	120.6(2)
C_3—H_9	111.2	110.1	106.5	106.6	107.0	109.6[h]
Bond angles						r_α
$C_5N_1C_2$	108.5	115.3	112.2	112.1	112.1	112.0(2)
$N_1C_2C_3$	107.2	102.7	104.7	104.8	105.4	106.8(2)
$N_1C_2O_6$	123.0	126.6	126.8	126.9	126.4	123.9(3)
$C_2C_3H_9$	123.2	123.2	121.9	121.9	122.2	114.7(3)

[a]Bond lengths in pm, bond angles in degrees, independent geometry parameters are listed for a planar molecular model of C_{2v} symmetry. See also Fig. 1 for numbering of atoms. [b]CNDO/2 fully optimized results [25]. [c]MNDO/3 fully optimized results [35], cited also in ref. 11. [d]Theoretical equilibrium geometry obtained with the 4-21 basis. [e]Theoretical equilibrium geometry obtained with the 4-21-N* basis. [f]Reference geometry obtained from r_e(4-21) by applying the empirical corrections suggested in ref. 26. [g]Experimental values (gas electron diffraction), see ref. 11. [h]Assumed values, kept fixed in the ED analysis.
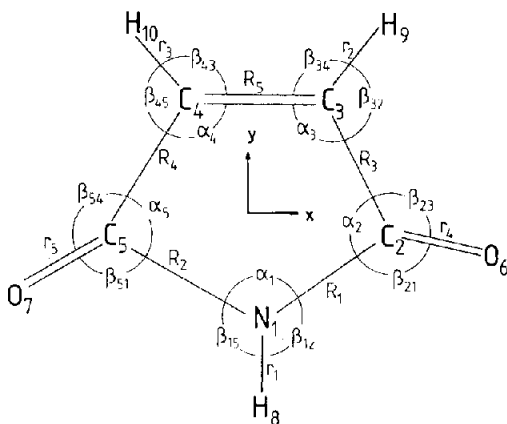

Fig. 1. Numbering of atoms and representation of in-plane internal coordinates of maleimide, coordinates used in the calculation are listed in Table 1.

given. The numbering of atoms follows Fig. 1. Both theoretical and electron diffraction results confirm the planarity of the molecule. Our main purpose concerning geometries is to obtain the best possible estimate of the true

equilibrium structure of MIM in order to use it as the reference geometry around which the energy surface is expanded. Both experimental and computational determinations of geometries are subject to errors, so exercise of judgement is required. As an indication of the importance of this step, we note that the CH stretching frequency shifts about 3% for 1 pm variation in the reference CH bond distance [5].

The 4-21 optimized geometry, corrected by standard offset values previously suggested [26], was chosen as the reference structure, r_{ref}. While the changes are small, it is believed that they produce a closer approximation to the true equilibrium structure. The correction to the N—C bond length is somewhat arbitrary and it may be that a small positive correction would have been preferable [9].

The only notable feature seen in a comparison of the data in Table 2 is the strong suggestion that the error in the electron diffraction value for the C_2—C_3—H_9 angle may be considerably larger than estimated. This is not surprising considering the difficulty of locating H atoms by this technique due to the low scattering power of H for electrons. The difference between our computed C—H and N—H bond lengths and those determined by experiment is an expected consequence of the difference between an r_g structure and the equilibrium structure. The semiempirical methods (CNDO and MINDO) are also parametrized to reproduce the vibrationally averaged results for bonds to H atoms and give C—H and N—H lengths appreciably longer than the r_e values.

Force field

The in-plane and out-of-plane SQM forcefields obtained from ab initio 4-21 calculations are given in Tables 3 and 4, respectively. The numerical values of the diagonal and relevant off-diagonal force constants are consistent with the conclusions on the rigidity and limited delocalization in the molecule of MIM derived from experimental [11] and CNDO/2 results [25, 36]. No important interaction between the N—C and C=C stretchings is observed (cf. $F_{\nu CN,\nu C=C}$ (MM) = 0.059 N m^{-1} vs. $F_{\nu CN,\nu CC,meta}$ (pyridine) = —0.419 N m^{-1} [5] calculated at the same ab initio level). Not only the endo-ring but also the exo-ring interactions ($F_{\nu C=O,\nu C=C}$ (MM) = —0.093 N m^{-1}) are very small in the O=C—C=C—C=O fragment. On the other hand, there is an important interaction between the two C=O stretchings ($F_{\nu C_4=O_6,\nu C_5=O}$ (MM) = 0.124 N m^{-1}) accompanied by significant interactions of νC=O with adjacent and non-adjacent ν_{CN} stretches (1.114 and —0.216 N m^{-1}, respectively). These couplings demonstrate that conjugation in MIM is not completely negligible and a small amount of delocalization is realized through the nitrogen in the ring.

The best comparison of different vibrational analyses is made at the level of the force constant matrices [1, 2]. Unfortunately, this is not possible for MIM since the published results of experimental studies [16, 21—23]

TABLE 3

In plane SQM forcefield for maleimide[a]

	r_1	r_2	r_3	r_4	r_5	R_1	R_2	R_3	R_4	R_5	β_1	β_2	β_3	β_4	β_5	α_1	α_2
r_1	6.711																
r_2	−0.002	5.249															
r_3	−0.002	0.010	5.249														
r_4	−0.009	0.028	0.011	11.795													
r_5	−0.009	0.011	0.028	0.127	11.795												
R_1	0.036	−0.013	−0.044	1.114	−0.216	5.623											
R_2	0.036	−0.044	−0.013	−0.216	1.114	0.581	5.623										
R_3	−0.032	0.001	−0.004	0.576	−0.124	0.421	−0.065	4.174									
R_4	−0.032	−0.004	0.001	−0.124	0.576	−0.065	0.421	0.155	4.174								
R_5	−0.042	0.037	0.037	−0.093	−0.093	0.059	0.059	0.256	0.256	8.653							
β_1	0.000	0.005	−0.005	0.025	−0.025	0.046	−0.046	−0.030	0.030	0.000	0.411						
β_2	0.002	0.012	0.003	0.009	−0.014	−0.001	−0.015	0.088	0.038	−0.116	0.011	0.401					
β_3	0.002	0.003	0.012	−0.014	0.009	−0.015	−0.001	0.038	0.088	−0.116	−0.011	−0.008	0.401				
β_4	−0.024	0.014	−0.001	0.047	0.056	0.369	0.369	0.007	0.007	0.012	−0.046	0.035	0.025	0.949			
β_5	−0.024	−0.001	0.014	0.056	0.047	−0.171	−0.171	−0.139	−0.139	0.012	0.046	0.025	0.035	0.072	0.949		
α_1	−0.109	−0.036	−0.036	0.263	0.263	0.134	0.134	−0.286	−0.286	0.287	0.000	−0.077	−0.077	0.135	0.135	1.711	
α_2	0.000	0.099	0.099	0.189	0.189	−0.109	0.109	0.197	−0.197	0.000	0.088	0.011	−0.011	−0.065	0.065	0.000	1.525

[a]Units are consistent with energy measured in aJ, stretching coordinates in Å and bending coordinates in radians. The values listed are the directly calculated ab initio 4-21 values scaled with the optimized empirical factors (Set B of Table 5). For notation see Table 1.

TABLE 4

Out-of-plane SQM force field for maleimide[a]

	γ_1	γ_2	γ_3	γ_4	γ_5	τ_1	τ_2
γ_1	0.140						
γ_2	0.010	0.388					
γ_3	0.010	−0.083	0.388				
γ_4	−0.039	−0.018	−0.041	0.686			
γ_5	−0.039	−0.041	−0.018	−0.024	0.686		
τ_1	0.000	0.162	−0.162	0.002	−0.002	0.280	
τ_2	−0.106	−0.027	−0.027	0.066	0.066	0.000	0.219

[a] See footnotes of Table 3.

do not give exact definitions of the coordinate systems that were used and it is therefore not possible to transform the experimental force fields to a common set of internal coordinates. In contrast, it is interesting to compare the SQM-CNDO/2 [25] and SQM-ab initio force constants. The two force fields agree reasonably well, e.g., the average difference between the in-plane force constants calculated by CNDO/2 and ab initio is 6.5%. More important differences are, of course, observed for coordinates βNH and νCC for which the corresponding experimental frequencies used in the fitting procedure in the two calculations were not the same. It should be noted that agreement between the SQM-CNDO/2 and ab initio out-of-plane force constants is less satisfactory though the absolute difference (nearly uniformly $\cong 0.05$ aJ rad^{-2}) seems to be acceptably good.

Scale factors

The scale factors used for the empirical corrections of the ab initio 4-21 force field of MIM are listed in Table 5. Set A contains the recommended values of the scale factors [27], established by simultaneous treatment of a series of small molecules and can be considered as a set of standard values for such systems. Set B shows the scale factors derived when the 4-21 force constants obtained in the present calculation were independently scaled to the experimental spectrum of MIM [16].

It is important to note that the scale factors are corrections for the use of a finite basis set and neglect of electron correlation in the computations. The entire procedure is based on the observation that such errors are similar for comparable vibrational modes in similar molecules. The computed force field corrected with Set A (Table 5) gives the best a priori estimate of the force field of MIM obtainable at this level of calculation without reference to any experimental data on MIM. Set B gives the best force field currently available by a combination of the calculations and the experimental data.

TABLE 5

Scale factors used for the empirical correction of the 4-21 ab initio force field maleimide

Internal coordinate	Scale factor[a]	
	Set A	Set B
In-plane		
ν_{NH}	0.880[b]	0.844
ν_{CH}	0.866	0.835
$\nu_{C=O}$	0.826	0.818
ν_{NC}	0.880[b]	0.878
ν_{CC}	0.920	0.901
$\nu_{C=C}$	0.866	0.869
β_{NH}	0.800[b]	0.790
β_{CH}	0.800	0.785
$\beta_{C=O}$	0.836	0.875
α_{ring}	0.800[b]	0.793
Out-of-plane		
γ_{NH}	0.500[c]	0.510
γ_{CH}	0.730	0.697
$\gamma_{C=O}$	0.800[b]	0.831
τ_{ring}	0.800[b]	0.731

[a]Set A: standard set of ref. 27; set B: optimized scale factors. See Table 1 for notation o of coordinates. [b]Approximate values obtained from the assumption that stretching and bending force constants are overestimated by 12% and 20%, respectively, in ab initio calculations using 4-21 basis set (cf. refs. 1—4). [c]Assumed value based on unpublished studies on pyrrole, imidazole and pyrazole.

Assignments

The relevant gas-phase experimental and the calculated fundamental frequencies are compiled in Table 6. The table contains some new assignments which are discussed in more detail below.

The first attempt to reproduce the vibrational fundamentals was to apply the theoretical 4-21 F-matrix scaled by the standard scale factors (Set A of Table 5) in the GF-method. Reasonable agreement with the completely a priori prediction was obtained (weighted mean deviations of 19.5 cm^{-1} and 12.3 cm^{-1} for the in- and out-of-plane fundamentals, respectively). On this basis, doubts arose concerning the assignment of two in-plane modes ($\nu_3(a_1)$, symmetric $\nu_{C=O}$ stretching, and $\nu_{19}(b_2)$, β_{NH}) and an out-of-plane mode ($\nu_{16}(b_1)$), ring torsion) because of the excessive disagreement between the predicted and the previously assigned frequencies. In fact, the region of the $\nu_{C=O}$ stretchings is noted for its character of being influenced by Fermi resonances. The broad band observed in the gas phase splits into 7 separate bands in Ar-matrix [19, 24] and the assignment of any of these bands to the fundamentals might be argued. Formerly, the band at 1775 cm^{-1} was assigned to $\nu_3(a_1)$ [16, 19]. It appears as a shoulder on a broad band of the

TABLE 6

Calculated and experimental vibrational frequencies (in cm^{-1}) for maleimide

Assign. description[a]	Ab initio			CNDO/2[d]	MINDO/3[e]	Experimental[f]		
	A^b	B^b	I_{abs}^c			[16]	[19]	[22]
a_1 species								
ν_1 100 ν_{NH}	3554	3482	67	3482	3483	3482 s	3482 s	3493
ν_2 98 ν_{CH}	3170	3114	2	3112	3093	3090 vw	3090 vw	—
ν_3 80 $\nu_{C=O}$	1810	1801	20	1782	1790	1775 sh	1775 sh	—
ν_4 82 $\nu_{C=C}$	1581	1582	0	1582	1578	1580 w	1580 w	—
ν_5 44 ν_{NC} + 26 $\beta_{C=O}$	1323	1326	190	1320	1278	1335 s	1330 s	1330
ν_6 83 β_{CH}	1061	1053	8	997	1086	1062 sh	—	1060
ν_7 69 ν_{CC}	896	889	1	910	990	897 s	—	—
ν_8 62 α_1	632	630	7	632	633	639 vw	637 vw	—
ν_9 71 $\beta_{C=O}$	390	396	31	381	392	—	—	—
a_2 species[g]								
ν_{10} 100 γ_{CH}	959	940	—	944	917	(954)[g]	—	—
ν_{11} 74 $\gamma_{C=O}$ + 28 ν_1	758	758	—	788	759	(773)[g]	—	—
ν_{12} 85 τ_1 + 24 $\gamma_{C=O}$	297	288	—	256	289	(295)[g]	—	—
b_1 species								
ν_{13} 50 γ_{CH} + 44 $\gamma_{C=O}$	847	841	454	846	884	831 s	831 s	831
ν_{14} 50 γ_{CH} + 34 $\gamma_{C=O}$	644	638	200	620	617	—	620 m	—
ν_{15} 97 γ_{NH}	499	503	195	504	505	620 m	504 s	622
ν_{16} 81 τ_2 + 22 $\tau_{C=O}$	175	169	58	63	161	—	—	—
b_2 species								
ν_{17} 99 ν_{CH}	3148	3091	1	3093	3111	—	—	—
ν_{18} 77 $\nu_{C=O}$	1760	1751	813	1748	1732	1756 vs	1756 vs	—
ν_{19} 63 β_{NH}	1342	1336	17	1402	1322	1322 s	—	—
ν_{20} 67 β_{CH}	1303	1292	0	1325	1267	1285 w	1285 w	1132
ν_{21} 37 ν_{CN} + 16 β_{CH}	1144	1142	36	1154	1142	1130 s	1130 s	1060
ν_{22} 37 ν_{CN} + 21 ν_{CC}	916	914	18	905	936	906 s	906 s	907
ν_{23} 61 α_2 + 27 ν_{CC}	679	675	29	674	667	668 s	668 s	675
ν_{24} 77 $\beta_{C=O}$	532	540	2	552	544	504 s	514 sh	—

[a] Description is based on the elements of the M matrix [34] obtained in scaling with Set B factors. Contributions less than 20% are omitted. For notation of the internal coordinates see Fig. 1 and Table 1. [b] Calculated from force constants scaled by scale factors. Sets A and B of Table 5, respectively. The weighted mean deviations (in cm^{-1}) are:

	Set A	Set B
in-plane	19.5	6.8
out-of-plane	12.3	9.6

For details see text.

[c] Absolute intensities in km mol^{-1} calculated from the dipole moment derivatives with respect to the internal coordinates. [d] Ref. 25, calculated using a scaled CNDO/2 force field. [e] Ref. 35, calculated using a scaled MNDO/3 force field. [f] Only relevant gas-phase data are listed, although other data are also available in the cited references. Notations used to characterize the experimental relative intensities: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder. [g] Normal modes of a_2 symmetry are inactive in the infrared, the experimental frequencies listed are taken from Raman data recorded in CH_3CN solution [16].

gas-phase spectra and is observed as a quite separate band in the melt and in the solid state. In these condensed phases, the splitting of the two $\nu_{C=O}$ frequencies, $\Delta = \nu_3 - \nu_{18}$, is of the order of 50 cm^{-1} [16], a value also

predicted by the ab initio calculations with set A scale factors. Accordingly, we believe that a band at a frequency of $\nu_{18} + 50 \approx 1800$ cm^{-1} should be assigned to ν_3, i.e., the band at 1795 cm^{-1} recorded in the gas-phase spectra [17, 19]. The band at 1775 cm^{-1} might be described as an overtone or a combination band, e.g.; $1775 \approx 2\,\nu_7 = 1778$ cm^{-1} (A$_1$); $1775 \approx \nu_8 + \nu_{21} = 1772$ cm^{-1} (B$_1$).

A similar consideration suggests that the band at 1340 cm^{-1}, instead of that at 1322 cm^{-1} [16], should be taken as the ν_{19} (b$_2$) fundamental. As a matter of fact, it is supposed, based on experimental evidence [19, 20, 24], that the asymmetric ν_{19} (b$_2$) fundamental should appear at higher wavenumbers than does ν_5 (a$_1$). From this assignment, and based on our calculations, we suggest that the peaks at 1322 cm^{-1} and 1335 cm^{-1} [16] should not be considered as separate fundamentals but as two branches of the same band of B-type contour. Their mean values should best approximate ν_5 (a$_1$). This supposition is also consistent with other available gas-phase [19, 22] and Ar-matrix data [19]. In the out-of-plane region, the predicted frequency of the ν_{16} (b$_1$) torsional mode was very low by using CNDO/2 [25]. Ab initio calculations permit the assignment of the band at 163 cm^{-1} observed in benzene solution [16] as this fundamental.

In all other cases ab initio and CNDO/2 [25] assignments are in agreement, and corroborate the assignment of Le Gall and co-workers [19, 20, 24]. For example, here again, the γ_{NH} out-of-plane bending is found to be at a lower frequency (504 cm^{-1}) than the 620 cm^{-1} assignment proposed by other authors [16]. In this work the band at 620 cm^{-1} is assigned to ν_{14} (b$_1$) and that at 504 cm^{-1} to ν_{15} (b$_1$).

Special mention should be made of the CH stretching region (around 3100 cm^{-1}). Ab initio calculations, scaled with set B, predict the ν_2 (a$_1$) and ν_{17} (b$_2$) fundamentals at 3114 and 3091 cm^{-1}, respectively. According to the usual expectations, ν_{17} (b$_2$) should be at the higher frequency but our ab initio calculation yields the opposite order. No support can be drawn from the gas-phase or condensed-state spectra since the ν_{CH} bands are weak and are practically hidden by noise. Only one fundamental is experimentally given in the infrared [16]. The spectra of the deuterated derivatives investigated here (all of C_{2v} symmetry, see below) have the same features as those of MIM, only asymmetric deuteration could have brought experimental evidence. In the absence of such experimental data, one is either driven to propose that the symmetry of the bands is inverted compared to the usual situation in the ν_{CH} region or, more probably, to ascribe the discrepancy to inadequacy of the present ab initio calculations. In the latter case, the sign of the $F_{\nu C_3 H_4, \nu C_4 H_{10}}$ cross-term should be considered as erroneous and changed.

Table 7 lists the frequencies of the most commonly studied isotopomers having C_{2v} symmetry (1-d_1; 3,4-d_2; 1,3,4-d_3 and ^{15}N). The available experimental frequencies [16, 18, 19, 21] for these molecules, however, do not permit a complete, separate analysis as for MIM-d_0, the parent molecule,

TABLE 7

Calculated and experimental vibrational frequencies for some C_{2v} isotopomers of maleimide[a]

Assign.		Calc.	1-d_1				3,4-d_2		1,3,4-d_3		^{15}N	
			Exp.				Calc.	Exp. solid[d]	Calc.	Exp. solid[d]	Calc.	Exp. solid[f]
			Vap.[b]	Solid[c]	Solid[d]	Matr.[e]						
In-plane												
a_1	ν_1	2558	2600	2368	2370	2595	3482	3210	2558	2400	3474	3201
	ν_2	3114	—	3105	3100	—	2330	2360	2330	2371	3113	3160
	ν_3	1801	—	1769	1770	1772	1799	1769	1799	1775	1801	1771
	ν_4	1581	—	1578	1578	1575	1531	1538	1531	1538	1581	1580
	ν_5	1313	1324	1338	1340	1326	1319	1343	1304	1338	1317	1368
	ν_6	1051	1059	1062	1065	1065	776	775	774	776	1052	1068
	ν_7	878	—	888	888	886	874	886	862	874	880	—
	ν_8	628	—	641	646	635	616	630	615	630	628	—
	ν_9	394	—	414	415	—	392	412	390	411	394	—
b_2	ν_{17}	3091	—	3097	3111	—	2283	2346	2283	2320	3091	3098
	ν_{18}	1741	—	1690	1700	1747	1750	1703	1739	1708	1750	1704
	ν_{19}	1225	1218	1204	1208	1219	1335	1368	1226	1223	1322	1350
	ν_{20}	1293	—	1300	1302	1299	1188	1192	1158	1170	1290	1300
	ν_{21}	1073	—	1085	1087	1072	1048	1140	971	1056	1139	1154
	ν_{22}	812	831	837	836	830	836	860	767	750	905	—
	ν_{23}	655	670	666	666	651	663	678	638	658	675	—
	ν_{24}	523	520	538	540	519	499	510	490	504	539	—
Out-of-plane												
a_2	ν_{10}	940	—	972	970	—	806	819	806	811	940	—
	ν_{11}	758	—	773	773	—	690	723	690	720	758	—
	ν_{12}	286	—	300	291	—	261	279	261	272	288	—
b_1	ν_{13}	841	797	850	850	800	793	—	792	—	840	—
	ν_{14}	637	—	518	628	619	524	710	514	520	635	—
	ν_{15}	371	—	—	520	—	491	—	369	—	502	—
	ν_{16}	167	—	175	—	—	168	172	166	—		

[a]Frequencies in cm^{-1}. The numbering of the fundamentals corresponds to Table 6.
[b]Ref. 22. [c]Ref. 16. [d]Ref. 21. [e]Ref. 19. [f]Ref. 18.

since the majority of the data are reported for the solid state. The only exception is the N-deuterated MIM for which a gas-phase spectrum is given [16]. Even this spectrum is of restricted use, as no frequencies are shown above 1800 cm^{-1} and only 8 or the 24 fundamentals are explicitly listed. The available gas-phase fundamentals agree with the calculations except for ν_1 (a$_1$) (discrepancy ca. 40 cm^{-1}) which, in its turn, is missing from the published spectrum. The other experimental (crystalline state, KBr pellet) frequencies can be compared only in the case of fundamentals not involving the NH or C=O fragments in the normal mode due to extensive H-bonding in condensed phases. These experimental studies may help, however, if isotopic shifts are compared. The shifts, e.g., for ^{15}N-MIM [18], agree with

the calculated differences of the respective fundamentals of MIM (Table 6) and ^{15}N-MIM (Table 7) acceptably. The comparison of the calculated fundamentals of MIM and its isotopomers (Table 6 and 7) reflects the effects of isotopic substitution. Deuteration yields, especially if compared to the ^{15}N-substitution, very significant shifts: in the case of MIM-d_1 from ca. 120 (ν_{15}) to ca. 920 (ν_1), and for MIM-d_2 from ca. 300 cm^{-1} (ν_6) to ca. 800 cm^{-1} (ν_2 and ν_{17}).

Effect of level of calculation

Certain force constants (Table 8) were calculated with a larger basis set (4-21-N*, d functions on N) because of the well-known difficulty of obtaining an adequate description of the electronic distribution around the nitrogen atom if polarization functions are not included in the basis set [37]. A thorough examination of the effect of basis size and electron correlation on the accuracy of the computed force constants has been made [38]. It has been shown that accurate results are obtainable by direct calculation only for very small molecules involving no more than three or four atoms. Reliable results for larger molecules must be based on scale corrections, as used in this work. Table 8 serves mainly to demonstrate the great importance of using scale factors derived at the exact level of calculation used for the unknown molecule. We believe that there is little to be gained, in general, by going to a computational level higher than Hartree—Fock calculations with the 4-21 basis set.

Some interesting observations about scaled semi-empirical force field calculations are also possible. In spite of the fact that the unscaled force constants obtained directly in such calculations are greatly in error, the

TABLE 8

Basis set effect on the force constants of maleimide

Internal coordinates		Force constant, F_{q_1,q_2} [a]	
q_1	q_2	4-21	4-21-N*
ν_{NH}	ν_{NH}	7.948	8.433
β_{NH}	β_{NH}	0.521	0.499
γ_{NH}	γ_{NH}	0.274	0.135
τ_1	τ_1	0.383	0.387
τ_2	τ_2	0.300	0.296
γ_{NH}	$\gamma_{C=O}$	−0.060	−0.045
ν_{NH}	ν_{NC}	0.042	0.076
ν_{NH}	$\nu_{C=C}$	−0.049	−0.033
ν_{NH}	α_1	−0.133	−0.103
β_{NH}	ν_{NC}	0.054	0.028
β_{NH}	ν_{CC}	−0.035	−0.028

[a]Theoretical unscaled values. For units see Table 3.

consistency of the error (and consequently, the validity of the scaling method) appears to be perhaps surprisingly good. The published scaled CNDO/2 force field for MIM [25] agrees remarkably well with the scaled ab initio force field reported here. The scaled CNDO/2 force field reported for uracil [39] also appears fully consistent with the present results. Work on a series of molecules [40—43] has also demonstrated the scaled CNDO/2 force fields and computed vibrational frequencies are good approximations of the ab initio ones. The example of pyridine [5, 40] is particularly clear in showing how useful scaled CNDO/2 force constants can be in establishing the major characteristics of the infrared spectrum and also, on the other hand, where its limits are in predicting some off-diagonal elements. For correct information, regarding the latter, and for a closer approach to experimental observations, the scaled ab initio results are necessary [3]. The semiempirical calculations require much less computer time, of course, but the cost of ab initio computation for molecules of the size considered here is insignificant in comparison with the effort required for a thoughtful analysis.

CONCLUSIONS

Previous studies on many molecules have demonstrated the wide applicability of the scaling procedure in structural and vibrational analyses [1—9]. The results presented here for maleimide lend additional confidence in the reliability of the technique.

On the basis of the scaled ab initio force field, a few of the assignments of vibrational fundamental frequencies can be confidently altered. It may be noted that such changes are in agreement with earlier CNDO/2 studies, although at that time there was not sufficient confidence in semi-empirical results to suggest these alterations of the assignments given in the experimental analyses.

Having accepted the validity of the general scaling concept, many authors choose a highly simplified procedure and merely take an arbitrary constant (e.g., 0.9) to multiply ab initio frequencies to get frequencies of an acceptable order of magnitude (see, for example, ref. 44). It is easy to see that within this concept one supposes that the forms of the normal modes (i.e., the relative atomic displacements in a mode as described by the vibrational eigenvectors) are correctly predicted and only the potential surface is to be reduced (or enlarged) uniformly. (In other words, scaling the force constants with one unique factor affects only the vibrational eigenvalues while the eigenvectors remain unaltered.) While such a procedure avoids a great deal of effort, we believe that it disregards much of the information content of the results. In the case of MIM, for example, use of the single factor 0.9 would yield a mean deviation between the experimental and calculated in-plane frequencies of about 50 cm^{-1}, while the standard set of scale factors [27] yields 20 cm^{-1}. This difference is highly significant when one comes to seeking out the major discrepancies which may indicate erroneous assignments.

After correction for such error and optimizing scale factors for MIM itself, the standard deviation of fundamental frequencies was reduced to 6.8 cm^{-1}. Optimization on the molecule under study is of value to obtain the best possible forcefield from combined theoretical and experimental evidences.

ACKNOWLEDGEMENT

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