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Vibrational analysis of the inelastic neutron scattering spectrum of pyridine

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Abstract

A vibrational analysis of the pyridine molecule has been performed by combining inelastic neutron scattering (INS) data and quantum mechanical calculations at the RHF, MP2 and B3LYP levels, with the 6-31G** and 6-311G** basis sets. Firstly, in order to test which level of theory is the best in reproducing the INS profile, this was calculated from the atomic displacement matrix of the pyridine molecule. DFT proved to be the most suitable option reproducing the above-mentioned spectrum, for both wave numbers and intensities. Secondly, in order to approximate the calculated spectrum to the observed one, the initial force constants matrix calculated at the B3LYP/6-311G** level was symmetrized using a set of independent symmetry coordinates (C_{2v}). All the diagonal and some off-diagonal force constants were fitted until the difference between observed and calculated spectra was minimized. Good agreement between both calculated and experimental INS spectra supports the validity of our 'empirical' (or effective) force field. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Although pyridine cannot be found in nature as such, its skeleton is present in many natural products such as vitamin B₆ (pyridinol), nicotine and more complex systems as DNA. The vibrational spectrum of this molecule has been studied for many years, from both experimental [1–20] and theoretical [21–27] points of view. This molecule has C_{2v} symmetry, with 27 normal modes distributed by symmetry species as $10A_1+3A_2+5B_1+9B_2$. Most of the vibrational modes have been assigned,

but the assignment of some out-plane modes, which appear in the low energy region, remains unclear. In this sense, inelastic neutron scattering (INS) is a very suitable technique due to the high spectral intensity in this region and the activity of optically silent modes.

As stated in previous works [28–30], in order to achieve an accurate vibrational analysis of the INS spectrum of the pyridine molecule, the initial force constants matrix calculated theoretically is symmetrized, and later refined by fitting the calculated INS spectrum to that recorded, by adjustment of the force constants. One interesting aspect in this analysis is the use of independent symmetry coordinates in the resolution of the secular equation, all of them having been built by orthogonality with

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the redundancies. The use of these kind of coordinates lets us express the force constants in the canonical form, and therefore allows us to compare and transfer them among similar molecules with physical meaning [31].

2. Experimental

The INS spectrum was obtained using the TFXA spectrometer at the ISIS pulsed neutron source, in the Rutherford Appleton Laboratory, Chilton, UK, which has an energy resolution $<2\%$. The counting time for the sample was 24 h. The sample was wrapped in aluminium foil and loaded into a standard liquid-helium cryostat controlled at $T < 20$ K. The low temperature is required to sharpen the vibrational fundamental bands and to decrease the intensity of the phonon wings.

3. Computational details

The force field and INS intensity calculations were performed using the CLIMAX program [32], which produces $S(Q, \omega)$ intensities taking full account of the Debye–Waller factor for the fundamentals, overtones and combinations. By default, the wave numbers and atomic displacements are calculated from the force constant matrix using the GF-Wilson method [33] without anharmonic corrections. The INS spectral intensities are calculated according to the theory given by Tomkinson et al. [34,35].

The program GAUSSIAN 94 [36] was used to carry out the ab initio and DFT calculations running on a Digital Alpha Server 2000. Calculations were performed using standard gradient techniques at the HF, MP2 and DFT (using Becke's three-parameter functional with correlation for exchange in conjunction with the non-local correction of Lee et al. to correlation, i.e. B3LYP) [37,38] levels using the 6-31G** and 6-311G** basis sets [39]. Vibrational wave numbers were calculated from analytic second derivatives to check the minimum on the potential energy surface.

The force constants obtained from the B3LYP/6-311G** calculation were used as a starting point

to set up an harmonic force field in symmetry coordinates, according to C_{2v} symmetry, using the CLIMAX program. To achieve this, a set of non-redundant coordinates according to C_{2v} symmetry were obtained by diagonalizing \mathbf{BB}^t and following the Schmidt procedure [40]. Such symmetry coordinates are listed in Table 1. The numbering of the atoms and internal coordinates are shown in Fig. 1. These symmetry coordinates were then used to diagonalize the secular equation and therefore to block out the subsequent vibrational analysis.

4. Results and discussion

4.1. Theoretical INS spectrum from ab initio and DFT calculations

One of the first steps in the INS analysis is to calculate the INS intensity from the atomic displacements matrix calculated via ab initio or DFT. This simple calculation can indicate the most suitable level of theory by which the INS feature could be reproduced. Fig. 2 shows the calculated spectrum for four different levels of theory, B3LYP/6-311G**, B3LYP/6-31G**, MP2/6-31G** and HF/6-31G**. As can be seen, the discrepancy between observed and calculated spectra is acceptable for the DFT methods, where observed intensities and wave numbers are close to those calculated. However, the discrepancy is more serious for the ab initio methods. Therefore, the next step would be to fit the initial force field until the difference between observed and calculated spectra is minimized, as done in previous works [28–30]. In this sense, we have chosen the B3LYP/6-311G** level of theory as starting point in the refinement procedure because it gives better agreement between calculated and observed wave numbers than the B3LYP/6-31G** one.

4.2. Force field refinement in symmetry coordinates

In general, our assignments are in agreement with those of Stidham and DiLella [11–14], and Wong and Colson [17,18], which have been recently confirmed in Ref. [41], and they have been

Table 1
Independent symmetry coordinates

Block	Symmetry coordinates	Primitive coordinates ^a
A ₁	$S_1^0 = S_1$	$S_1 = 1/\sqrt{2}(r_1 + r_5)$
	$S_2^0 = S_2$	$S_2 = 1/\sqrt{2}(r_2 + r_4)$
	$S_3^0 = S_3$	$S_3 = r_3$
	$S_4^0 = S_5$	$S_4 = 1/\sqrt{2}(R_1 + R_6)$
	$S_5^0 = -0.708 S_4 - 0.706 S_6 + 8.891 \times 10^{-6} S_7$	$S_5 = 1/\sqrt{2}(R_2 + R_5)$
	$S_6^0 = 0.238 S_8 - 0.708 S_9 + 0.665 S_{10}$	$S_6 = 1/\sqrt{2}(R_3 + R_4)$
	$S_7^0 = 8.877 \times 10^{-6} S_6 + 0.705 S_7 - 0.668 S_8 + 3.989 \times 10^{-4} S_9 + 0.239 S_{10}$	$S_7 = \alpha_1$
	$S_8^0 = 0.499 S_4 - 0.500 S_6 - 0.290 S_7 - 0.203 S_8 + 0.204 S_9 + 0.289 S_{10}$	$S_8 = 1/\sqrt{2}(\alpha_2 + \alpha_6)$
	$S_9^0 = S_{11}$	$S_9 = 1/\sqrt{2}(\alpha_3 + \alpha_5)$
	$S_{10}^0 = S_{12}$	$S_{10} = \alpha_4$
		$S_{11} = 1/\sqrt{2}(\beta_1 - \beta_5)$
		$S_{12} = 1/\sqrt{2}(\beta_2 - \beta_4)$
	$R_1 = -0.305 S_4 + 0.306 S_6 - 0.625 S_7 - 0.631 S_8 - 0.136 S_9 + 0.080 S_{10} \equiv 0$	
	$R_2 = -0.272 S_4 + 0.272 S_6 - 0.010 S_7 + 0.211 S_8 + 0.652 S_9 + 0.618 S_{10} \equiv 0$	
B ₂	$S_{11}^0 = S_{13}$	$S_{13} = 1/\sqrt{2}(r_1 - r_5)$
	$S_{12}^0 = S_{14}$	$S_{14} = 1/\sqrt{2}(r_2 - r_4)$
	$S_{13}^0 = -0.700 S_{15} + 0.714 S_{17}$	$S_{15} = 1/\sqrt{2}(R_1 - R_6)$
	$S_{14}^0 = -0.707 S_{18} + 0.707 S_{19}$	$S_{16} = 1/\sqrt{2}(R_2 - R_5)$
	$S_{15}^0 = -0.861 S_{16} + 0.360 S_{18} + 0.360 S_{19}$	$S_{17} = 1/\sqrt{2}(R_3 - R_4)$
	$S_{16}^0 = 0.670 S_{15} - 0.176 S_{16} + 0.657 S_{17} - 0.211 S_{18} - 0.211 S_{19}$	$S_{18} = 1/\sqrt{2}(\alpha_2 - \alpha_6)$
	$S_{17}^0 = S_{20}$	$S_{19} = 1/\sqrt{2}(\alpha_3 - \alpha_5)$
	$S_{18}^0 = S_{21}$	$S_{20} = 1/\sqrt{2}(\beta_1 + \beta_5)$
	$S_{19}^0 = S_{22}$	$S_{21} = 1/\sqrt{2}(\beta_2 + \beta_4)$
		$S_{22} = \beta_3$
	$R_3 = -0.247 S_{15} - 0.478 S_{16} - 0.243 S_{17} - 0.571 S_{18} - 0.571 S_{19} \equiv 0$	
A ₂	$S_{20}^0 = 0.704 S_{23} - 0.709 S_{24} + 0.041 S_{26}$	$S_{23} = 1/\sqrt{2}(\gamma_2 - \gamma_6)$
	$S_{21}^0 = 0.047 S_{23} + 0.392 S_{25} - 0.818 S_{26} + 0.418 S_{27}$	$S_{24} = 1/\sqrt{2}(\gamma_3 - \gamma_5)$
	$S_{22}^0 = 0.618 S_{23} + 0.615 S_{24} - 0.364 S_{25} + 0.028 S_{26} + 0.326 S_{27}$	$S_{25} = 1/\sqrt{2}(\tau_1 + \tau_6)$
		$S_{26} = 1/\sqrt{2}(\tau_2 + \tau_5)$
		$S_{27} = 1/\sqrt{2}(\tau_3 + \tau_4)$
B ₁	$R_4 = 0.347 S_{23} + 0.342 S_{24} + 0.583 S_{25} - 0.032 S_{26} - 0.649 S_{27} \equiv 0$	
	$R_5 = -0.006 S_{23} - 0.039 S_{24} - 0.611 S_{25} - 0.572 S_{26} - 0.546 S_{27} \equiv 0$	
B ₁	$S_{23}^0 = 0.724 S_{28} + 0.690 S_{29}$	$S_{28} = 1/\sqrt{2}(\gamma_2 + \gamma_6)$
	$S_{24}^0 = -0.704 S_{31} + 0.710 S_{33}$	$S_{29} = 1/\sqrt{2}(\gamma_3 + \gamma_5)$
	$S_{25}^0 = -0.923 S_{30} + 0.384 S_{32}$	$S_{30} = \gamma_4$
	$S_{26}^0 = 0.590 S_{28} - 0.619 S_{29} + 0.368 S_{31} + 0.365 S_{33}$	$S_{31} = 1/\sqrt{2}(\tau_1 - \tau_6)$
	$S_{27}^0 = -0.282 S_{28} + 0.296 S_{29} - 0.236 S_{30} + 0.479 S_{31} - 0.567 S_{32} + 0.479 S_{33}$	$S_{32} = 1/\sqrt{2}(\tau_2 - \tau_5)$
		$S_{33} = 1/\sqrt{2}(\tau_3 - \tau_4)$
	$R_6 = 0.220 S_{28} - 0.231 S_{29} - 0.303 S_{30} - 0.373 S_{31} - 0.728 S_{32} - 0.370 S_{33} \equiv 0$	

^a $\beta_i = 1/\sqrt{2}(\phi_i - \phi'_i)$.

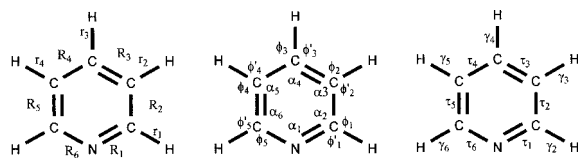


Fig. 1. Internal coordinates as defined for pyridine.

taken as a reference in the present work. Observed and calculated wave numbers are listed in Table 2.

As usual, it is not possible to assign experimentally the C–H stretching modes around 3000 cm⁻¹ from the INS spectrum, and therefore the only available data for this region come from the IR and/or Raman spectra [41], and they have been included as the experimental data in the refinement procedure. For the rest of in-plane modes, all of them are already assigned without controversy, and we have confirmed the previous assignments [11–14,17,18,41] in this work.

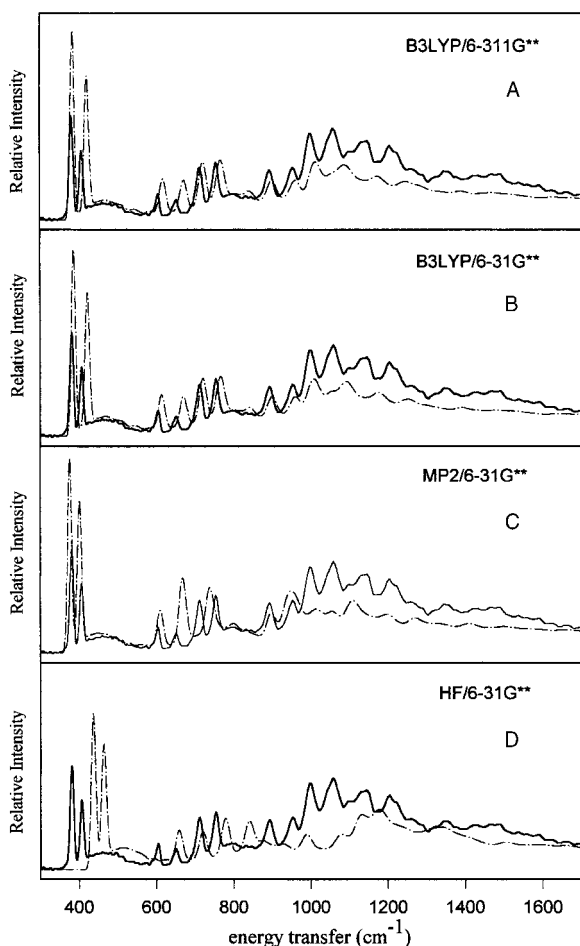


Fig. 2. Observed (—) and calculated (---) INS spectra of pyridine from the vibrational wave numbers and atomic displacements: (A) at the B3LYP/6-311G** level, (B) at the B3LYP/6-31G** level, (C) at the MP2/6-31G** level, and (D) at the HF/6-31G** level.

For the out-plane modes, however, a greater uncertainty exists since the assignments for the ν_{10a} and ν_{16a} (A_2 symmetry) and ν_5 and ν_{10b} (B_1 symmetry) have been repeatedly modified. In this sense, taking into account the assignments that appeared in Ref. [41], which is close to those of Stidham and DiLella [11–14] and Wong and Colson [17,18], and the calculated values at the B3LYP/6-311G** level, we have proposed an initial assignment for each out-plane mode in the INS spectrum. It must be noted that we have assigned

ν_5 to the strong band at 1005 cm^{-1} in the INS spectrum. This mode was only observed and assigned by Stidham and DiLella [11–14] to a weak band in the Raman spectrum at 1007 cm^{-1} , and we corroborate that here.

Finally, in order to confirm our assignment proposal, all the diagonal and some off-diagonal force constants were refined arriving at a good reproduction of the INS profile for the wave numbers and intensities as well. Initially, only the wave number data were used to refine the diagonal force constants in each symmetry block. Later, the INS intensities were included to determine the most important off-diagonal force constants so that the INS profile could be reproduced. Initial and final force constants can be found in Table 3, with observed and calculated wave numbers in Table 2.

The calculated INS spectrum after the refinement is compared with that observed in Fig. 3. The distribution of the phonon wings has been fitted using a single parameter, which describes the external-mode Debye–Waller factor, with a final value of 0.023, this being similar to those for other azines [28–30].

It is interesting to compare our force field, which is based on the INS spectrum, with those obtained by other authors. We have chosen the last force field calculated by Wiberg et al. [27] because we consider this to be the most reliable. Thus, we have transformed the force constants given in Ref. [27] into our independent symmetry coordinates system. To achieve this, we have used the expression proposed by Martínez et al. [31], which allows us to transform the force constants matrix, \mathbf{F}_j , referred to the j -system of independent coordinates, into another i -system of independent coordinates, \mathbf{F}_i , as follow:

$$\mathbf{F}_i = (\mathbf{B}_i \mathbf{B}_i^t)^{-1} \mathbf{B}_i \mathbf{B}_j^t \mathbf{F}_j \mathbf{B}_j \mathbf{B}_i^t (\mathbf{B}_i \mathbf{B}_i^t)^{-1} \quad (1)$$

where $\mathbf{B} = \mathbf{U} \mathbf{b}$, \mathbf{U} being the orthogonal matrix relating the independent symmetry coordinates to the dependent internal ones, \mathbf{b} is the matrix relating the internal coordinates to the cartesian coordinates, and \mathbf{B}^t is the transpose of the \mathbf{B} matrix. The force constants obtained after the transformation are listed in Table 4. As can be seen, the

Table 2

Observed, calculated and refined vibrational wave numbers for pyridine-h₅ (cm⁻¹)

Mode	B3LYP/ 6-311G**	IR, Raman ^a	INS	Refined	PED
A₁					
ν_2	3192	3090	3090	3089	30 S_1 + 42 S_2 + 24 S_3
ν_{13}	3168	3078	3078	3075	53 S_1 + 42 S_3
ν_{20a}	3146	3052	3052	3057	14 S_1 + 51 S_2 + 31 S_3
ν_{8a}	1626	1581	1581	1582	36 S_4 + 17 S_5
ν_{19a}	1512	1482	1482	1482	41 S_8 + 22 S_9 + 16 S_{10}
ν_{9a}	1241	1216	1210	1209	14 S_8 + 45 S_9
ν_{18a}	1093	1072	1058	1058	18 S_8 + 48 S_{10}
ν_{12}	1047	1030	1030	1030	34 S_6 + 24 S_7
ν_1	1010	991	991	991	17 S_4 + 39 S_5
ν_{6a}	617	603	603	603	27 S_6 + 42 S_7
B₂					
ν_{20b}	3183	3033	3033	3034	46 S_{11} + 53 S_{12}
ν_{7b}	3143	3025	3025	3018	53 S_{11} + 43 S_{12}
ν_{8b}	1619	1574	1574	1580	51 S_{13} + 13 S_{19}
ν_{19b}	1472	1437	1437	1437	11 S_{13} + 23 S_{15} + 14 S_{17} + 14 S_{18} + 11 S_{19}
ν_{14}	1384	1355	1350	1355	59 S_{17} + 16 S_{18} + 16 S_{19}
ν_3	1282	1227	1227	1230	18 S_{15} + 41 S_{16}
ν_{15}	1170	1146	1138	1137	21 S_{16} + 28 S_{18} + 27 S_{19}
ν_{18b}	1077	1068	1047	1045	33 S_{15} + 10 S_{16} + 21 S_{18}
ν_{6b}	670	653	653	654	78 S_{14}
A₂					
ν_{17a}	1004	984	984	984	30 S_{20} + 45 S_{22}
ν_{10a}	899	881	895	895	15 S_{21} + 31 S_{22}
ν_{16a}	384	374	380	380	16 S_{20} + 67 S_{21}
B₁					
ν_5	1017	1007	1005	1005	54 S_{23} + 15 S_{24} + 12 S_{25} + 12 S_{27}
ν_{10b}	959	942	948	948	18 S_{26} + 59 S_{27}
ν_4	765	748	748	748	17 S_{23} + 13 S_{24} + 51 S_{25} + 12 S_{26}
ν_{11}	720	701	710	710	11 S_{23} + 59 S_{26}
ν_{16b}	421	406	406	406	67 S_{24} + 21 S_{25}

^a Ref. [41].

diagonal force constants resulting from the INS refinement are similar to those obtained by Wiberg et al. [27], but larger differences are obtained for the off-diagonal force constants. This fact is not surprising given the sensitivity of INS intensities to the off-diagonal terms. Further, we started from a different level of theory than that of Wiberg et al.

Finally, we have calculated the IR spectrum from the atomic displacements for each normal mode, corresponding to the final force field, and the atomic charges calculated at the B3LYP/6-311G** level following the procedure given in Ref. [33]. For this, we have used the CLIMAX program by which the calculated IR intensity is simulated

by a Gaussian profile. We have only performed a qualitative comparison between the observed and calculated infrared spectra. In Fig. 4, we show the calculated IR spectrum along with the corresponding observed one in gas phase. As can be seen, there exists good correspondence between the observed and calculated spectrum except for those modes <500 cm⁻¹, and those between 900 and 1300 cm⁻¹, where the calculated IR intensity from our force field is higher than the observed one. The reason for these discrepancies could be due to the fact that the experimental IR spectrum is for the gas phase sample, and the calculated INS spectrum comes from the solid state sample.

Table 3
Force constants ($\text{aJ } \text{\AA}^{-2}$) in symmetry coordinates for the pyridine molecule after the refinement procedure^a

A₁									
$F_{1,1}$	5.189(5.441)								
$F_{2,2}$	0.011	5.128(5.507)							
$F_{3,3}$	0.004	0.015	5.172(5.531)						
$F_{4,4}$	0.107	0.086	0.014	7.200(7.204)					
$F_{5,5}$	-0.176	-0.021	-0.089	-0.456	7.528(8.147)				
$F_{6,6}$	-0.071	0.086	-0.138	-0.143	-0.123				
$F_{7,7}$	0.115	-0.151	-0.016	-0.317	-0.518	1.228(1.299)			
$F_{8,8}$	0.179	-0.291	-0.104	-0.101	-0.266	-0.041	1.319(1.393)		
$F_{9,9}$	0.047	-0.004	0.012	0.193	0.248	-0.025	0.268	5.927(7.149)	
$F_{10,10}$	0.000(0.001)	0.330	-0.009	-0.148	-0.136	-0.043	-0.109	-0.216	0.555(0.605)
						0.064	0.086	-0.106	0.009
									0.452(0.507)
B₂									
$F_{11,11}$	5.025(5.434)								
$F_{12,12}$	0.007	4.977(5.511)							
$F_{13,13}$	-0.209	0.046	7.264(7.489)						
$F_{14,14}$	0.113	-0.202	0.557	1.374(1.476)					
$F_{15,15}$	-0.122	0.015	0.109	-0.049	4.604(4.797)				
$F_{16,16}$	0.207	-0.006	-0.159	-0.036	-0.508	4.036(4.438)			
$F_{17,17}$	0.057	-0.015	0.212	-0.005	-0.104	-0.212	0.570(0.588)		
$F_{18,18}$	0.002	0.307	0.186	0.058	0.086	0.097	0.005	0.471(0.485)	
$F_{19,19}$	-0.012	-0.001	-0.182	-0.084	0.023	-0.127	-0.016	0.013	0.520(0.524)
A₂									
$F_{20,20}$	0.268(0.320)								
$F_{21,21}$	0.046(0.065)	0.278(0.273)							
$F_{22,22}$	0.039	0.021	0.367(0.331)						
B₁									
$F_{23,23}$	0.423(0.304)								
$F_{24,24}$	-0.011	0.302(0.287)							
$F_{25,25}$	0.003	-0.003(-0.029)	0.251(0.337)						
$F_{26,26}$	0.000(0.025)	0.020(0.025)	-0.016(-0.028)	0.271(0.334)					
$F_{27,27}$	-0.010	-0.002	-0.032	0.062	0.306(0.302)				

^aThe initial values are in parentheses for those force constants which have been refined.

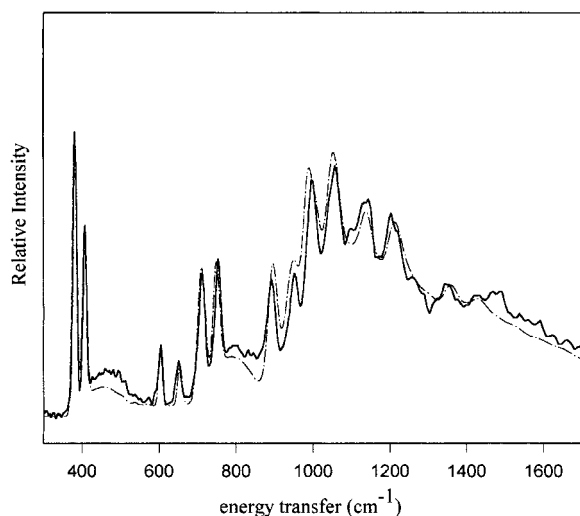


Fig. 3. Observed and calculated INS spectra of pyridine after refinement of symmetrized force constants. The conventions of this figure are as for Fig. 2.

5. Conclusions

The INS spectrum of the pyridine molecule has been analyzed confirming the previous assignments for the in-plane vibrational modes of the molecule and clarifying the ambiguities for the out-plane ones [11–14,18,41]. For this, the force constants matrix in symmetry coordinates calculated at the B3LYP/6-311G** level has been taken as initial force field. Later, all the diagonal and some off-diagonal force constants were fitted up to the difference between the observed and calculated spectra was minimized. In order to check the validity of our final force field, the IR spectrum was calculated from the final force field, with reasonable results. In addition, the force constants obtained by Wiberg were expressed in our coordinates system in order to compare both force fields, obtaining similar results for the diagonal force constants and bigger differences for the off-diagonal force constants, as expected.

The combined use of *ab initio* calculations with INS spectroscopy provides a powerful tool in the analysis of molecular vibrations. The subsequent use of empirical adjustment allows transferable force constants to be obtained, which can be used to analyse spectra of similar molecular units in less

Table 4

Comparison of the force constants matrix from this work and that by Wiberg et al. [27]^a

Potential energy term	Ref. [27]	This work
$F_{1,1}$	5.054	5.189
$F_{2,1}$	0.016	0.011
$F_{2,2}$	5.218	5.128
$F_{3,1}$	0.004	0.004
$F_{3,2}$	0.017	0.015
$F_{3,3}$	5.159	5.172
$F_{4,1}$	0.070	0.107
$F_{4,2}$	0.035	0.086
$F_{4,3}$	−0.040	−0.014
$F_{4,4}$	6.946	7.200
$F_{5,1}$	−0.063	−0.176
$F_{5,2}$	0.014	−0.021
$F_{5,3}$	−0.039	−0.089
$F_{5,4}$	−0.377	−0.456
$F_{5,5}$	7.866	7.528
$F_{6,1}$	−0.061	−0.071
$F_{6,2}$	0.138	0.086
$F_{6,3}$	−0.103	−0.138
$F_{6,4}$	−0.224	−0.143
$F_{6,5}$	−0.124	−0.123
$F_{6,6}$	1.302	1.228
$F_{7,1}$	0.092	0.115
$F_{7,2}$	−0.031	−0.151
$F_{7,3}$	−0.004	−0.016
$F_{7,4}$	−0.284	−0.317
$F_{7,5}$	−0.547	−0.518
$F_{7,6}$	−0.044	−0.041
$F_{7,7}$	1.239	1.319
$F_{8,1}$	0.075	0.179
$F_{8,2}$	−0.022	−0.291
$F_{8,3}$	−0.062	−0.104
$F_{8,4}$	0.104	−0.101
$F_{8,5}$	−0.247	−0.266
$F_{8,6}$	−0.035	−0.025
$F_{8,7}$	0.304	0.268
$F_{8,8}$	6.729	5.927
$F_{9,1}$	0.058	0.047
$F_{9,2}$	−0.003	−0.004
$F_{9,3}$	0.010	0.012
$F_{9,4}$	0.172	0.193
$F_{9,5}$	0.225	0.248
$F_{9,6}$	−0.047	−0.043
$F_{9,7}$	−0.096	−0.109
$F_{9,8}$	−0.226	−0.216
$F_{9,9}$	0.583	0.555
$F_{10,1}$	−0.001	0.000
$F_{10,2}$	−0.032	0.330
$F_{10,3}$	−0.011	−0.009
$F_{10,4}$	−0.182	−0.148
$F_{10,5}$	−0.139	−0.136
$F_{10,6}$	0.061	0.064
$F_{10,7}$	0.087	0.086

(continued on next page)

Table 4 (continued)

Potential energy term	Ref. [27]	This work
$F_{10,8}$	−0.109	−0.106
$F_{10,9}$	0.001	0.009
$F_{10,10}$	0.503	0.452
$F_{11,11}$	5.088	5.025
$F_{12,11}$	0.012	0.007
$F_{12,12}$	5.180	4.977
$F_{13,11}$	−0.109	−0.209
$F_{13,12}$	0.046	0.046
$F_{13,13}$	7.069	7.264
$F_{14,11}$	0.082	0.113
$F_{14,12}$	−0.079	−0.202
$F_{14,13}$	0.458	0.557
$F_{14,14}$	1.362	1.374
$F_{15,11}$	−0.089	−0.122
$F_{15,12}$	−0.056	0.015
$F_{15,13}$	0.148	0.109
$F_{15,14}$	−0.114	−0.049
$F_{15,15}$	4.736	4.604
$F_{16,11}$	0.117	0.207
$F_{16,12}$	0.037	−0.006
$F_{16,13}$	−0.337	−0.159
$F_{16,14}$	−0.002	−0.036
$F_{16,15}$	−0.520	−0.508
$F_{16,16}$	3.943	4.036
$F_{17,11}$	−0.058	0.057
$F_{17,12}$	0.001	−0.015
$F_{17,13}$	−0.182	0.212
$F_{17,14}$	−0.003	−0.005
$F_{17,15}$	0.089	−0.104
$F_{17,16}$	0.181	0.212
$F_{17,17}$	0.563	0.570
$F_{18,11}$	0.001	0.002
$F_{18,12}$	0.038	0.307
$F_{18,13}$	−0.128	0.186
$F_{18,14}$	−0.057	0.058
$F_{18,15}$	−0.101	0.086
$F_{18,16}$	−0.092	0.097
$F_{18,17}$	0.006	0.005
$F_{18,18}$	0.485	0.471
$F_{19,11}$	0.010	−0.012
$F_{19,12}$	−0.010	−0.001
$F_{19,13}$	0.159	−0.182
$F_{19,14}$	0.075	−0.084
$F_{19,15}$	−0.012	0.023
$F_{19,16}$	0.115	−0.127
$F_{19,17}$	−0.013	−0.016
$F_{19,18}$	0.012	0.013
$F_{19,19}$	0.517	0.520
$F_{20,20}$	0.469	0.268
$F_{21,20}$	0.238	0.046
$F_{21,21}$	0.281	0.278
$F_{22,20}$	0.003	0.039
$F_{22,21}$	0.003	0.021
$F_{22,22}$	0.322	0.367

Table 4 (continued)

Potential energy term	Ref. [27]	This work
$F_{23,23}$	0.373	0.423
$F_{24,23}$	−0.164	−0.011
$F_{24,24}$	0.280	0.302
$F_{25,23}$	0.080	0.003
$F_{25,24}$	−0.156	−0.003
$F_{25,25}$	0.478	0.251
$F_{26,23}$	0.011	0.000
$F_{26,24}$	0.025	0.020
$F_{26,25}$	−0.205	−0.016
$F_{26,26}$	0.699	0.271
$F_{27,23}$	0.008	−0.010
$F_{27,24}$	−0.009	−0.002
$F_{27,25}$	−0.024	−0.032
$F_{27,26}$	0.086	0.062
$F_{27,27}$	0.129	0.306

^a Units are consistent with energy measured in aJ, stretching and bending coordinates in Å and radian, respectively.

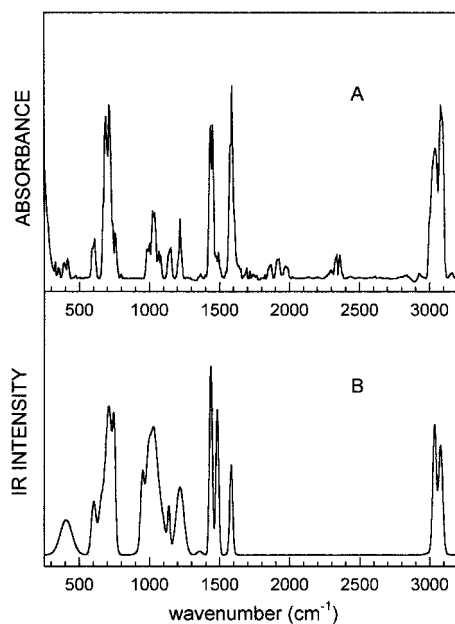


Fig. 4. Observed (A) and calculated (B) IR spectra of the pyridine molecule.

tractable environments. It should be noted, however, that where intermolecular interactions are strong, the initial ab initio calculation will give poor agreement with the observed spectrum, and attempts to make up for these discrepancies by

force-constant refinement is not meaningful and is unlikely to reproduce the observed INS spectrum.

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References

- [1] J. Turkevich, P.C. Stevenson, *J. Chem. Phys.* 11 (7) (1943) 328.
- [2] C.H. Kline, J. Turkevich, *J. Chem. Phys.* 12 (7) (1944) 300 and references therein.
- [3] L. Corrin, B.J. Fax, R.C. Lord, *J. Chem. Phys.* 21 (7) (1953) 1170.
- [4] J.K. Wilmshurst, H.J. Bernstein, *Can. J. Chem.* 35 (1957) 1183.
- [5] J.P. McCullough, D.R. Douslin, J.F. Messerly, I.A. Hosselopp, T.C. Kincheloe, G. Waddington, *J. Am. Chem. Soc.* 79 (1957) 4289.
- [6] D.A. Long, F.S. Murfin, E.L. Thomas, *Trans. Faraday Soc.* 59 (1963) 12.
- [7] D.A. Long, E.L. Thomas, *Trans. Faraday Soc.* 59 (1963) 783.
- [8] J. Loisel, V. Lorenzelli, *J. Mol. Struct.* 1 (1967–1968) 157.
- [9] E. Castellucci, G. Sbrana, F.D. Verderame, *J. Chem. Phys.* 51 (9) (1969) 3762.
- [10] Y. Kakiuti, M. Akiyama, N. Saito, H. Saito, *J. Mol. Spectrosc.* 61 (1976) 164.
- [11] H.D. Stidham, D.P. DiLella, *J. Raman Spectrosc.* 8 (3) (1979) 180.
- [12] D.P. DiLella, H.D. Stidham, *J. Raman Spectrosc.* 9 (2) (1980) 90.
- [13] D.P. DiLella, *J. Raman Spectrosc.* 9 (4) (1980) 239.
- [14] H.D. Stidham, D.P. DiLella, *J. Raman Spectrosc.* 9 (4) (1980) 247.
- [15] M.S. Afifi, A. Shabana, *Analysis* 10 (5) (1982) 239.
- [16] Y. Ozono, Y.N. Maehara, H. Shimada, R. Shimada, *Bull. Chem. Soc. Jpn* 59 (1986) 1617.
- [17] K.N. Wong, S.D. Colson, *J. Phys. Chem.* 87 (1983) 2102.
- [18] K.N. Wong, S.D. Colson, *J. Mol. Spectrosc.* 104 (1984) 129.
- [19] V.A. Walters, D.L. Snavely, S.D. Colson, K.B. Wiberg, K.N. Wong, *J. Phys. Chem.* 90 (1986) 592.
- [20] T.D. Klots, *Spectrochim. Acta A* 54 (1998) 1481.
- [21] M.A. Kovner, Yu.S. Korostelev, V.I. Berezin, *Opt. Spectrosc.* 9 (1960) 233.
- [22] V.I. Berezin, *Opt. Spectrosc.* 15 (1963) 167.
- [23] G. Zerbi, B. Crawford, J. Overend, *J. Chem. Phys.* 38 (1) (1963) 127.
- [24] S. Suzuki, W.J. Orville-Thomas, *J. Mol. Struct.* 37 (1977) 321.
- [25] L. Harsányi, F. Kilár, *J. Mol. Struct.* 65 (1980) 141.
- [26] G. Pongor, P. Pulay, G. Fogarasi, J.E. Boggs, *J. Am. Chem. Soc.* 106 (1984) 2765.
- [27] K.B. Wiberg, V.A. Walters, K.N. Wong, S.D. Colson, *J. Phys. Chem.* 88 (1984) 6067.
- [28] A. Navarro, J.J. López González, G.J. Kearley, J. Tomkinson, S.F. Parker, D.S. Sivia, *Chem. Phys.* 200 (1995) 395.
- [29] G.J. Kearley, J. Tomkinson, A. Navarro, J.J. López-González, M. Fernández-Gómez, *Chem. Phys.* 216 (1997) 323.
- [30] A. Navarro, M.P. Fernández Liencres, M. Fernández-Gómez, J.J. López-González, E. Martínez, J. Tomkinson, G. Kearley, *J. Phys. Chem.* 103 (1999) 5833.
- [31] E. Martínez, J.J. López-González, M. Fernández-Gómez, *J. Chem. Phys.* 110 (1999) 3302.
- [32] G. Kearley, *J. Chem. Soc. Faraday Trans. II* 82 (1984) 41.
- [33] E.B. Wilson Jr., J.C. Decius, P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
- [34] J. Howard, C.B. Boland, J. Tomkinson, *Chem. Phys.* 777 (1983) 145.
- [35] J. Tomkinson, M. Warner, A.D. Taylor, *Mol. Phys.* 51 (1984) 381.
- [36] M. Frish, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, *GAUSSIAN 94*, Review B.1, Gaussian Inc., Pittsburgh, 1995.
- [37] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [38] A.D.J. Becke, *Chem. Phys.* 98 (1993) 5648.
- [39] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.
- [40] G. Zerbi, in: A.J. Barnes, M.J. Orville-Thomas (Eds.), *Vibrational Spectroscopy-Modern Trends*, Elsevier, Amsterdam, 1977.
- [41] F. Partal, M. Fernández Gómez, J.J. López González, submitted for publication.