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REASSIGNMENT OF THE FUNDAMENTAL VIBRATIONS OF AZETIDINE FROM *AB INITIO* CALCULATIONS

PER HALFDAN NIELSEN*

Marine Chemistry Section, Department of General and Organic Chemistry, The H. C. Ørsted Institute,
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

AND

MICHAEL GAJHEDE

Chemical Laboratory IV, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

ABSTRACT

The harmonic vibrational frequencies were calculated analytically at the 6-31** level for azetidine using the GAUSSIAN 82 program. The results strongly indicate the presence of several errors in a recent assignment of the fundamentals of azetidine based on a normal coordinate analysis and a revised assignment is suggested. It is concluded that reliable vibrational data for azetidine in the gas phase are needed in order to resolve the remaining ambiguities in the interpretation of the spectra.

During work on the structure and vibrational spectra of 3-azetidinol,[1] it became increasingly clear that it was impossible to obtain a vibrational assignment of the fundamentals compatible with the reported interpretations of the IR and Raman spectra of azetidine. Even the recent assignment by Günther *et al.*,[2] based on gas-phase IR and Raman spectra and supported by a full normal coordinate analysis, appeared to contain gross errors. Thus, for example, the NH deformation frequencies in azetidine were assigned bands at 1321 cm^{-1} (species A') and 1088 cm^{-1} (species A'') whereas in the related aziridine the corresponding values are firmly established as 998 cm^{-1} (A') and 1237 cm^{-1} (A'').[3] *Ab initio* methods at the DZP level[4] have been shown to give an excellent account of the fundamentals of strained systems such as aziridine, provided that the calculated frequencies are multiplied by an approximately constant factor close to 0·9.

Since the decisive feature seems to be flexibility and inclusion of polarization functions in the valence shell, the 6-31** basis set was chosen for a provisional reassignment of the azetidine spectrum. The calculations were made at the SCF level using the analytical gradient method via full geometry optimization with 161 primitive and 95 contracted basis functions. The

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*Author for correspondence.

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molecule was restricted to transform according to point group C_s. The total energy of the optimized structure was −172.091759214 a.u. and the zero-point vibrational energy 67.11386 kcal mol^{-1}. Recently,[5] an identical treatment has proved very helpful in analyzing the lowest normal modes in azetidine connected with pyramidal inversion at nitrogen. Since this lends strong support to the validity of the calculation, we decided to extend it to a comparison of all the fundamental vibrations.

The gas-phase IR spectrum has been reported twice.[2,6] Very recently careful investigations of the region below 700 cm^{-1} have revealed[7] that hot bands of the ring puckering mode at 208 cm^{-1} obscure the fundamental at 648 cm^{-1}. This was not noted by Günther *et al.*,[2] who assigned instead two fundamentals to the latter region. The gas-phase Raman spectrum has only been illustrated once, but without a list of the frequencies.[8] Unfortunately, Günther *et al.*[2] did not give any of their gas-phase Raman data. However, Raman frequencies in the liquid state, with complete[6] and partial[9] polarization data, have been reported.

In Table 1 the calculated harmonic frequencies (cm^{-1}) are listed for azetidine and compared with previous[2,6] and revised assignments. The ratio between the experimental and calculated

Table 1. Vibrational assignment for azetidine[a]

				Revised assignment			
Species	ν	Exp[2]	Exp[6]	Exp	Calc	Exp/Calc	Dominating mode[b]
A'	1	3359	3362	3359	3789	0·887	NH str
	2	3004	3003	3004	3284	0·915	CH_2 as str
	3	2975	2989	2975	3238	0·919	CH_2 as str
	4	2947	2959	2947	3225	0·914	CH_2 s str
	5	2862	2933	2862	3163	0·905	CH_2 s str
	6	1499	1469	1499	1677	0·894	δCH_2
	7	1450	1450	1450	1620	0·895	δCH_2
	8	1321	1253	1321	1501	0·880	wCH_2
	9	1253	1145	1253	1330	0·942	tCH_2
	10	1145	1028	1145	1279	0·895	$iNH + \rho CH_2$
	11	1029	950	1029	1129	0·911	CN s str
	12	950	913	950	1034	0·919	ρCH_2
	13	892	892	892	1009	0·884	CC s str
	14	736	825	736	822	0·895	$\rho CH_2 + iNH$
	15	662	735	648	710	0·913	δring
	16	200	–	208	222	0·937	ring pucker
A''	17	2960	2989	2960	3230	0·916	CH_2 as str
	18	2934	2959	2934	3157	0·929	CH_2 s str
	19	1341	1495	1469	1648	0·891	δCH_2
	20	1245	1341	1341	1522	0·881	δNH
	21	1137	1242	1245	1407	0·885	wCH_2
	22	1088	1199	1199	1402	0·855	wCH_2
	23	990	1137	1137	1314	0·865	tCH_2
	24	938	1088	1088	1218	0·893	tCH_2
	25	912	990	990	1112	0·890	CN as str
	26	860	925	912	1005	0·907	CC as str
	27	650	–	814	897	0·907	ρCH_2

[a] Exp = experimental values, with reference numbers where relevant; Calc = calculated values.

[b] Abbreviations: str = stretching; as = asymmetric; s = symmetric; δ = deformation; w = wagging; t = twisting; ρ = rocking; i = inversion

values for the revised set of fundamentals serves as an index of agreement. Finally, an approximate description of the normal modes is given. The CH/NH stretching frequencies have been transferred from the paper by Günther *et al.*,[2] since the resolving power of the instrument used by Lippert and Prigge[6] obviously was not sufficient to clarify the complicated pattern observed in this region. The calculated values suggest a reassignment of ν_{18} (A'') to the same region as ν_5 (A'). The two lowest A' fundamentals have been unambigously identified by Egawa and Kuchitsu[7] at 208 and 648 cm^{-1}. Both previous assignments are based on combined IR and Raman data and agree that bands at 1450, 1253, 1145, 1029, 950, 892 and 736 cm^{-1} are definitely of species A', whereas those at 1341, 1245, 1137, 1088 and 990 cm^{-1} should be assigned species A''. Since all these bands (with the exception of the 1253 cm^{-1} band) can be fitted well with the calculated values, they have been included in the revised list of fundamentals. This defines the ratio between experimental and calculated frequencies to be ca 0·90. The validity of the assignment of the remaining bands, two of species A' and four of species A'', will be discussed in some detail below.

The CH$_2$ scissoring vibrations can be assigned in harmony with the extensively investigated trimethylene oxide[10] (A_1, 1505 and 1452 cm^{-1}; B_1, 1480 cm^{-1}) to bands in the 1450–1500 cm^{-1} region in azetidine. However, there is no agreement[2,6] regarding the interpretation of the gas-phase contours in the infrared of the band near 1500 cm^{-1} and the available Raman evidence for the bands in question can also be taken to support both species. The proposed assignment (A', 1499 cm^{-1}; A'', 1469 cm^{-1}) may therefore have to be reversed. Doubtless the CH$_2$ scissoring vibration of species A'' cannot be attributed the band at 1341 cm^{-1} as proposed by Günther *et al.*[2] On the other hand, we agree with their assignment of ν_8 (A') to the 1321 cm^{-1} band, as also indicated by the calculations.

Two fundamentals of species A'' are predicted near 1250 cm^{-1} but only one is observed. In the gas-phase IR spectra another very weak band can be discerned at 1197 cm^{-1}, and the Raman spectrum of liquid azetidine shows a medium band at 1199 cm^{-1} which is depolarized.[6] In the solid-state Raman spectrum this is observed[9] as a medium to strong doublet near 1204 cm^{-1} and a band near 1190 cm^{-1} is also clearly seen in the gas-phase Raman spectrum.[8] These facts make it highly unlikely that we are dealing with a combination mode or an overtone and the band is attributed the fundamental ν_{22} (A''), as proposed by Lippert and Prigge.[6] In the region predicted for the CH$_2$ rocking mode of species A'' three bands at 913, 925, and 944 cm^{-1} are observed in the gas-phase IR spectrum obtained by Lippert and Prigge,[6] whereas Günther *et al.*[2] observed two bands at 912 and 938 cm^{-1} with different band contours. In the gas-phase Raman spectrum only a broad band is found in this region.[8] However, in the liquid state a depolarized band of medium strength at 925 cm^{-1} is observed.[6] This gains intensity in the solid state[9] and is the likely candidate for ν_{26} (A''). The lowest fundamental of species A'' may be identified with the 860 cm^{-1} band in the gas-phase IR spectrum observed by Günther *et al.*,[2] probably corresponding to the three peaks at 844, 852 and 873 cm^{-1} described by Lippert and Prigge.[6] However, a counterpart has not been observed in the Raman spectra,[6,8,9] and we are therefore probably dealing with a combination mode involving ν_{16} and/or ν_{15}/ν_{27}. Since a band has been observed in both the IR and the Raman spectra[9] near 814 cm^{-1} corresponding to the calculated value of ν_{27} (A''), this has been included in Table 1 as a provisional assignment.

We conclude that the overall agreement between the theoretical and experimental values in Table 1 justifies the use of 6-31** *ab initio* calculations as a guide for assigning the fundamentals of azetidine. Moreover, we believe that these data have been useful in clarifying where ambiguities remain in the interpretation of the vibrational spectrum.

REFERENCES

1. U. Anthoni, C. Christophersen, P. H. Nielsen and M. Gajhede, *Acta Crystallogr.* submitted for publication.
2. H. Günther, G. Schrem and H. Oberhammer, *J. Mol. Spectrosc.* **104**, 152–164 (1984).
3. (a) W. J. Potts, *Spectrochim. Acta* **21**, 511–527 (1965); (b) K. Kalcher, W. Kosmus and K. Faegri, Jr, *Spectrochim. Acta, Part A* **34**, 889–893 (1981).
4. E. D. Simandiras, R. D. Amos, N. C. Handy, T. J. Lee, J. E. Rice, R. B. Remington and H. F. Schaefer III, *J. Am. Chem. Soc.* **110**, 1388–1393 (1988).
5. R. Dutler, A. Rauk and T. S. Sorensen, *J. Am. Chem. Soc.* **109**, 3224–3228 (1987).
6. E. Lippert and H. Prigge, *Ber. Bunsenges. Phys. Chem.* **67**, 554–560 (1963).
7. T. Egawa and K. Kuchitsu, *J. Mol. Spectrosc.* **128**, 469–477 (1988).
8. L. A. Carreira, R. O. Carter and J. R. Durig, *J. Chem. Phys.* **57**, 3384–3387 (1972).
9. J. Le Brument, J. Hoch and M. Jaffrain, *C. R. Acad. Sci., Ser. B* **269**, 752–755 (1969).
10. (a) R. A. Kydd, H. Wieser and W. Kiefer, *Spectrochim. Acta, Part A* **39**, 173–180 (1983); (b) G. Banhegyi, P. Pulay and G. Fogarasi, *Spectrochim. Acta, Part A* **39**, 761–769 (1983).