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# Vibrational spectra and conformation of methanal azine

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**Abstract**—Vibrational spectra, both infra-red absorption and Raman scattering, are presented for isotopic methanal azines,  $C_2H_4N_2$ ,  $C_2H_2D_2N_2$  and  $C_2D_4N_2$ , in both the vapour phase near 300K and the solid phase at 48–78K. A complete vibrational assignment for  $C_2H_4N_2$  is proposed, and a partial assignment for  $C_2D_4N_2$ . For  $C_2H_2D_2N_2$ , three structural isomers of HDCNNCHD, depending on relative position of deuterium substitution, are deduced to exist. The equilibrium nuclear conformation is proved to be the s-transoid structure. From intensity effects and rotational fine structure of the vapour spectra of  $C_2H_4N_2$  and  $C_2D_4N_2$ , Coriolis interactions are shown to occur; for  $C_2H_4N_2$ ,  $|\zeta_{1,17}| = 0.49 \pm 0.05$ .

### INTRODUCTION

METHANAL azine  $H_2C=N-N=CH_2$  is the simplest acyclic azine. Work previously published on this molecular species has included a brief report [1] which sketched its preparation and properties as an organic chemical, and another communication [2] which summarised some preliminary spectroscopic and photochemical results. Two further major articles have presented in some detail discussion of electronic spectra and photochemical processes [3] and reaction kinetics in flash photolysis [4], particularly involving the directly detected methyleniminyl free radical,  $H_2CN$ . Also the role of methanal azine in the photodecomposition of diazomethane has been outlined [5].

According to the brief articles [1, 2] alluded to above, vibrational and microwave spectra were interpreted to indicate that the equilibrium nuclear conformation of methanal azine was the s-cisoid diene form, unlike the related conjugated molecules butadiene-1,3, ethandial and propenal [6]. However rotational fine structure in the vibrational absorption establishes beyond doubt that the azine has the s-transoid conformation. Other spectroscopic data are on re-analysis found not only to be consistent with this structure but further to provide strong confirmation.

In this article we present vibrational spectra of methanal azine and deuterated analogues in vapour and solid phases. Analysis of these spectra establishes the conformation as well as indicating a vibration-rotational interaction not previously recognised to occur for these dienes.

# EXPERIMENTAL

Methanal azine was prepared [3] by depolymerisation of the dried white solid which was precipitated from solution when hydrazine (64% in  $H_2O$ ) reacted with

<sup>[1]</sup> N. P. NEUREITER, J. Am. Chem. Soc. 81, 2910 (1959).

<sup>[2]</sup> J. F. OGILVIE, Chem. Commun. 359 (1965).

<sup>[3]</sup> J. F. OGILVIE and D. G. HORNE, J. Chem. Phys. 48, 2248 (1968).

<sup>[4]</sup> D. G. HOBNE and R. G. W. NORRISH, Proc. Roy. Soc. A315, 301 (1970).

<sup>[5]</sup> J. F. OGILVIE, Photochem. Photobiol. 9, 65 (1969).

<sup>[6]</sup> R. K. HARRIS, Spectrochim. Acta 20, 1129 (1964).

methanal, either in formalin solution or as solid polyoxymethylene. The stoichiometry may be indicated by the equation:

 $N_2H_4 + 2H_2CO \rightarrow (H_2CNNCH_2)_{polymeric} + 2H_2O.$ 

In the case of the deuterated methanal azines, the corresponding deuterated polyoxymethylenes (Merck, Sharpe and Dohme, Montreal) were employed. Purification was effected by vacuum distillation and fractionation procedures. The purest product from the depolymerisation was obtained by utilising the smallest temperature at which permanent gas evolution through a liquid-nitrogen trapped collection system could be detected. Greater temperatures led to production of ammonia which proved difficult to separate. However, repeated distillation through a loosely packed column of solid metaphosphoric acid provided removal of ammonia with only minor contamination by water vapour.

Various grating spectrometers in the Cambridge University Chemical Laboratories, Division of Pure Chemistry of the National Research Council of Canada, and this laboratory were employed to record the spectra. The vapours were contained in conventional cells of 0.1 m or 1.25–8.75 m (folded) paths while the solids were frozen from the vapour in conventional single- or double-Dewar cryostats containing liquid or solid nitrogen. The spectrometers were calibrated with absorption bands of standard gases. A slightly non-linear scan of a Perkin–Elmer 225 spectrometer caused some difficulty in obtaining rotational constants of accuracy expected from the spectral resolution, but the corrections to individual lines (of the order of 0.1 cm<sup>-1</sup>) could not be made as much as desired because of the sparsity of calibration lines in regions of interest.

Full statistical analyses of results were conducted with programmes prepared for an Olivetti programmable calculator and an IBM 1620 computer.

#### RESULTS

# 1. Methanal- $h_2$ azine (C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>)

The vapour phase absorption spectrum is reproduced in Fig. 1. (The background of some weak broad bands from material deposited on the windows has been subtracted.) The broad band around  $380 \text{ cm}^{-1}$  has been confirmed, as have other weak bands, by recording with ordinate expansion during long scan periods. Solid phase spectra are presented in part in Fig. 2; an intense band at  $412 \text{ cm}^{-1}$  and several weak bands beyond 3675 cm<sup>-1</sup> do not appear within the range of Fig. 2. The solid phase scattered spectrum is presented in Fig. 3, in which the narrow peaks are attributed to Raman shifts but the broad underlying emission continuum is ascribed to some fluorescence effect. As the apparent Raman line at 490.5 nm moved and split slightly when excitation wavelength changed from 488.0 to 514.5 nm, this line is presumed to be an artefact at least as far as the intramolecular vibrations are concerned. An attempt to observe the scattered spectrum of the vapour at  $5 \text{ kNm}^{-2}$ pressure yielded a weak line corresponding to a Raman shift of 1615 cm<sup>-1</sup>, and also another line at 1335 cm<sup>-1</sup>. As there was some surface polymerisation contributing to light scattering, and as the 1335  $\text{cm}^{-1}$  shift in no way fits into the later analysis, it is no further considered. A full listing of wavenumbers, absorbances and (for



Fig. 1. Infrared absorption between 4000-300 cm<sup>-1</sup> of  $C_2H_4N_2$  vapour, 50 hN m<sup>-8</sup> pressure in 100 mm cell with KBr windows. Spectral slit width ~1.5-4 cm<sup>-1</sup>. Broken line about 400 cm<sup>-1</sup> indicates background of evacuated cell.



Fig. 2. Infrared absorption between (a)  $650-2160 \text{ cm}^{-1}$ , (b)  $2160-3675 \text{ cm}^{-1}$ , of solid  $C_2H_4N_2$ , thickness unmeasured, at 48K. Spectral slit width  $\sim 1-3 \text{ cm}^{-1}$ .

vapour absorption) band types is presented in Table 1. Assignments are discussed later.

# 2. Methanal-hd azine $(C_2H_2D_2N_2)$

Only vapour phase absorption spectra, as in Fig. 4, are available for the partially deuterated species. The listing of the data appears in Table 2.

Although there was considerable difficulty in preparing both the deuterated azines, methanal-hd azine proved the more difficult. The reason is believed to be that the polyoxymethylene-hd was much less reactive than  $(D_2CO)_n$ , because of



Fig. 3. Scattering emission from solid  $C_{2}H_{4}N_{2}$  at 78K, illuminated with argon ion laser at 488.0 nm. Abscissa is linear in wavelength from 600 to 485 nm.

Vapour		Solid					
Wavenumber	Absorbance	Band type	$(\nu_{calc})$	Wavenumber	Absorbance	(Veale)	Assignment
~380	weak	B?		412	>2		v <sub>18</sub>
				413	(Raman)		V18
				614	(Raman)		v,
				679	0.16		ν <sub>s</sub>
				851	(Raman)		νs
				855	0.01		ve
996 P	0.40)						
1019 Q	0.75 }	o		1054	>2		v.
1031 R	0.38)						
				1108	0.01	(1108)	$v_{L'} + v_{11}$
				1128	0.02	(1128)	$v_{s} + v_{L}$
1157 P 1176 R	$\{0.13\\0.185\}$	B		1187	>2		V <sub>17</sub>
				1218	(Raman)		ν
				1249	0.10	(1263)	$\nu_{e} + \nu_{1e}$
1390 P	0.29	A/B		1411	>2		¥16
1409 19	0.303			1497	(Remen)		<b>w</b> .
				1537	0.08	(1542)	v + v
1615 (Pomon)				1611	(Raman)	(2012)	V-
1010 (1900000)				1617	0.32	(1630)	$v_{-} + v_{-}$
1696 P	0.05)					()	
1637 0	0.04	AIR		1640	0.86		<b>V</b> 1r
1646 R	0.05						- 10
1010 10	0.00)					((1727)	$y_{0} + y_{11}$
				1726	0.13	or	
						(1726)	$v_0 + v_{10}$
				1908	0.24	(1905)	$v_a + v_a$
1972 P	0.035)					· ·	
1981 Q	0.04 }	A/B	(1995)	2008	0.06	(2023)	$v_2 + v_{18}$
1994 R	0.06	,					
2023 P	0.125)						
2033 Q	0.095	A B	(2033)	2102	1.35	(2102)	$v_{8} + v_{11}$
2044 R	0.11		-				
				2258	0.04	$\begin{cases} (2262) \\ or \end{cases}$	$v_6 + v_{16}$
						(2254)	$v_7 + v_{15}$
				2390	0.02	(2405)	$v_{5} + v_{17}$
				2485	0.055	(2491)	$v_6 + v_{15}$

Table 1. Absorption wavenumbers and Raman shifts for  $\mathrm{C}_{2}\mathrm{H}_{4}\mathrm{N}_{2}$ 

Table 1 (cont.)

Vapour Wavenumber Absorbance		Band type	(Veale)	Solid Wavenumber Absorbance		(Vcalc)	Assignment
2760 P	0.01						
2780 R	0.01}	B	(2781)	2768 2835	0.15 0.05	(2798) (2858)	$   \nu_{8} + \nu_{17} \\   \nu_{5} + \nu_{15} $
2934 P	0.87)						• • •
2943 Q	0.79}	A B		2924	0.90		¥14
2953 R	0.98)						
				2940	(Raman)		v <sub>2</sub>
3007	weak		(3014)		0.06	(3022)	$v_{8} + v_{18}$
3068 P	0.36						
3078 Q	0.31	A B		3057	1.15		V <sub>13</sub>
3088 R	0.39						
				3072	(Raman)		<i>v</i> <sub>1</sub>
3225 P	0.085						
3235 Q	0.07	A B	(3252)	3232	0.11	(3251)	$v_{3} + v_{15}$
3244 <i>R</i>	0.085						
				3376	0.05	(3337)	$v_{12} + v_{14}$
				3460	0.025	(3470)	$v_{12} + v_{13}$
				3677	0.02	(3671)	$v_7 + v_{13}$
				3915	0.03	(3908)	$v_6 + v_{13}$
				3972	0.06	(3972)	$v_{11} + v_{14}$
				4090	0.11	(4105)	$v_{11} + v_{13}$
				4143	0.05	(4142)	$v_{5} + v_{14}$
				4218	0.105	(4259)	$v_1 + v_{17}$
				4269	0.10	(4287)	$v_5 + v_{13}$
				4360	0.03	(4351)	$(v_4 + v_{14})$
							or
							$(v_2 + v_{16})$
				4430	0.05	(4483)	$v_1 + v_{16}$
				4460	0.15	(4484)	$v_4 + v_{13}$
				4520	0.26	(4535)	$v_{3} + v_{14}$
				4662	0.25	(4668)	$\nu_8 + \nu_{18}$
				4690	0.20	(4712)	$v_1 + v_{15}$
				6135	0.04	(6129)	$v_1 + v_{18}$

greater chain length or crystallinity, so that, under the conditions of synthesis on a small scale, only a partial conversion to the desired product was achieved. After relatively rapid scans of the vibration-rotational absorption, the product was consumed in the flash photolysis experiments [3] (after purification). Lack of availability of  $(\text{HDCO})_n$  precluded further synthesis of this azine. The curve in Fig. 4 has been drawn with omission of two absorptions due to two extraneous species, at 1180 and 1722 cm<sup>-1</sup>. The spectrum of HDCO, previously measured after an unsuccessful azine preparation, closely resembled the published spectra [7] except for two features. An additional weak band at 3424 cm<sup>-1</sup>, obviously of type-A contour with a  $\Delta(PR)$ -separation of ~50 cm<sup>-1</sup>, is easily assigned as the first overtone of the intense carbonyl valence-stretching fundamental of HDCO at 1722 cm<sup>-1</sup>. The other feature at 1180 cm<sup>-1</sup>, disappearing upon evacuation of the cell, can be attributed to neither HDCO nor the azine, but is probably due to s-trioxane, cyclic (HDCO)<sub>8</sub>.

# 3. Methanal-d<sub>2</sub> azine (C<sub>2</sub>D<sub>4</sub>N<sub>2</sub>)

Only absorption spectra are available for the fully deuterated azine, but for both vapour and solid phases, as shown in Figs. 5 and 6, respectively. Absorptions are listed in Table 3.

<sup>[7]</sup> D. W. DAVIDSON, B. P. STOICHEFF and H. J. BERNSTEIN, J. Chem. Phys. 22, 289 (1954).



Fig. 4. Infra-red absorption between  $3400-600 \text{ cm}^{-1}$  of  $C_2H_2D_2N_2$  vapour, 30 hN m<sup>-3</sup> pressure in 100 mm cell with NaCl windows. Spectral slit width ~1.5-2.5 cm<sup>-1</sup>. Broken line indicates deletion of bands of known impurities (HDCO and (HDCO)<sub>2</sub>).



938 Q; 952 Q; 965 Q; 1305; 1597 P, 1606 Q, 1614 R; 1853; 1905; 2204 P, 2224 R; 2257 P, 2277 R; 2980 P, 2990 Q, 3001 R; 3048 P, 3058 Q, 3067 R; 3170.



Fig. 5. Infrared absorption between 3800-650 cm<sup>-1</sup> of  $C_2D_4N_2$  vapour, 25 hN m<sup>-2</sup> pressure in 100 mm cell with NaCl windows. Spectral slit width ~1.5-3 cm<sup>-1</sup>. Some bands were scanned with ordinate expansion of 2-5 times.

#### DISCUSSION

As a basis for discussion of the presented spectra of methanal azines, the structure, or at least the conformation, must be established. Then the vibrational modes and wavenumbers can be classified. Finally the rotational fine structure, band contours and other intensity phenomena for the vapour phase can be considered. Actually, all of these topics are interrelated, but a partial separation is convenient for clarity.



Fig. 6. Infra-red absorption between (a) 650-2160, (b) 2160-3675 cm<sup>-1</sup>, of solid  $C_2D_4N_2$ , thickness unmeasured, at 48K. Spectral slit width  $\sim l-3$  cm<sup>-1</sup>.

Table 3. Absorptio	n wavenumbers	of	$C_{2}D_{1}$	<b>Λ</b> Ν,
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Vapour: 790 P, 811 Q, 820 R, v <sub>8</sub> ; 942 P, 962 R, v <sub>17</sub> ; 1025 P, 1036 Q, 1043 R, v <sub>16</sub> ; 15	71 P,
1580 Q, 1589 R, $v_{15}$ ; 1615 P, 1635 R, $v_6 + v_8$ ; 2173 P, 2182 Q, 2191 R, $v_{14}$ ; 2301 P, 23	20 R,
$v_{13}$ ; 3130 P, 3150 R, $v_3 + v_{15}$ ; 3750 P, 3770 R, $v_3 + v_{13}$ .	
Solid: 401; 470; 649; 675; 701; 743; 770; 786; 807; 830, v <sub>8</sub> ; 842; 961, v <sub>17</sub> ; 1004;	1015,
$1038, v_{16}; 1064; 1074; 1119; 1170; 1202; 1313; 1327; 1412; 1422; 1468; 1496;$	1546,
$1573, v_{15}; 1592; 1621; 1664, v_8 + v_8; 1679; 1725; 1827; 2015; 2073; 2113; 2140;$	2183,
$v_{14}$ ; 2258; 2305, $v_{13}$ ; 2340; 2345; 2517; 2645; 2860; 2932; 3023; 3062; 3104;	3125,
$v_3 + v_{15}$ ; 3241, $v_5 + v_{14}$ ; 3340, $v_1 + v_{16}$ ; 3363; 3371; 3407; 3470; 3741, $v_3 + v_{13}$ ;	3870,
$v_1 + v_{15}; 4575, v_1 + v_{13}.$	

# Conformation of methanal azine

The first report [1] of the synthesis of monomeric methanal azine claimed that the vapour phase infrared absorption was compatible with only an s-cisoid structure, (I) in Fig. 7, presumably on the basis of the apparent doubling of some bands, such as 6.04 and 6.12, 7.08 and 7.16, and 8.47 and 8.64  $\mu$ m. However, the spectrum of Fig. 1 makes plain that these pairs of bands are really just *R*- and *P*-branches of ordinary composite vibration-rotation bands. Perhaps also the reaction of methanal azine with hydrogen sulphide to form 1,3,4-thiadiazolidine (III) was taken to support the cisoid conformation. However butadiene-1,3 undergoes cyclisation and other reactions, possibly through a transition state more favourably formed from a *cis* rather than a *trans* rotational isomer, even though only the transoid rotamer is definitely characterised [6].



Fig. 7. Conformations of azines and related species. In (VIII),  $I_A$  and  $I_B$  are appropriately oriented when X = H or D.

Later evidence [2] interpreted in favour of the s-cisoid conformer (I) were both the presence of several bands in the C—H valence-stretching region and the apparent occurrence of overtones. Both of these properties would be incompatible with the greater symmetry ( $C_{2h}$  rather than  $C_{2v}$ ) of the centrosymmetric s-transoid rotamer. However further analysis led to the assignment of some of these bands as combinations of fundamental modes, other than the two obvious C—H fundamentals. The best clue to the correct conformation of methanal azine came from vibrationrotational spectra under improvided resolution. The band centred at 1019 cm<sup>-1</sup> bears a great resemblance, in shape, spacing of fine structure and relatively great intensity, to the 908 cm<sup>-1</sup> band of butadiene-1,3. All further rotational analysis yielded data compatible with only an s-transoid conformation, (II) in Fig. 7. Hence the following discussion will be based on this premise.

There is still the observed microwave absorption [2] to be explained. (Measurements were conducted for samples (at  $\sim 8 \text{ Nm}^{-2}$  pressure) in a conventional copper waveguide at 195K, using Stark modulation and oscilloscopic display.) Fairly intense lines at 27.940 and 28.750 GHz, both with Stark components at greater frequencies, and a series of weaker lines at 29.077, 29.220, 29.232, 29.247, 29.251, 29.260, 29.336, and 29.789 GHz were detected, in addition to a few weak lines recognised to belong to methanol and ammonia. Intensities of the specified lines decreased slowly during the period, some minutes, of measurement. All detectable satellites of these lines showed second-order Stark effects, indicative of their carrier being an asymmetric rotor. All lines were sharp, with no indication of nitrogen quadrupolar broadening. Thus the microwave lines are appropriate to a molecular species, if a single carrier be responsible for the set listed, having a hindered internal rotor, but not containing nitrogen atoms or other atoms with quadrupolar nuclei. An attempt to fit the frequencies with calculated rotational constants of a cisoid rotamer of reasonable structural parameters yielded a complete lack of correlation. Thus we conclude that these microwave signals are due to no form of methanal azine; the true carrier probably has a relatively large dipole moment and a fairly small barrier so some internal rotation.

### Vibrational analysis

For an s-transoid centrosymmetric planar equilibrium nuclear conformation of methanal- $h_2$  or  $-d_2$  azines, the eighteen fundamental intramolecular vibrations may be classified under point group  $C_{2h}$ :

$$\Gamma(C_{2h}) = 7A_g + 3A_u + 2B_g + 6B_u$$

As usual for a centrosymmetric molecule, the  $A_q$  and  $B_q$  vibrations are formally Raman active and infra-red inactive, whereas the  $A_u$  and  $B_u$  modes are Raman inactive and active in absorption. Twelve of the vibrations can be visualised to be simply those of a pair of H<sub>2</sub>CN fragments taken to be either symmetric or antisymmetric with respect to the inversion operation at the centre of symmetry. The other six vibrations then correspond essentially to motions, either rotational or translational, of one H<sub>2</sub>CN fragment relative to the other. Thus there are four C—H valence-stretching vibrations,  $v_1$  and  $v_2(A_g)$ , and  $v_{13}$  and  $v_{14}(B_u)$ ; two C=N stretching vibrations,  $r_{s}(A_{q})$  and  $r_{15}(B_{u})$ ; two methylene symmetric deformation (or scissoring) vibrations,  $r_4(A_g)$  and  $r_{16}(B_u)$ ; two methylene rocking vibrations (in the molecular plane),  $r_5(A_{\sigma})$  and  $r_{17}(B_u)$ ; and two methylene wagging vibrations (out of the molecular plane),  $v_{\theta}(A_u)$  and  $v_{11}(B_{\sigma})$ . As the N-N stretching vibration,  $v_{\theta}(A_{\sigma})$ ; two skeletal bending vibrations (in plane),  $r_7(A_a)$  and  $r_{18}(B_u)$ ; two skeletal wagging vibrations (out of plane),  $r_9(A_u)$  and  $r_{12}(B_q)$ ; and the torsional vibration,  $r_{10}(A_u)$ , all involve differential movement of essentially only the non-hydrogenic atoms, the corresponding vibration frequencies are expected to be smaller than all those of the preceding group of twelve.

There is only one uniquely defined axis in these  $C_{2\lambda}$  molecules, the z-axis or figure axis, perpendicular to the molecular plane and bisecting the N—N internuclear vector. As this axis must by symmetry coincide with the major inertial axis  $I_C$ , vibrationrotational bands with transition moment parallel to the z-axis, of  $A_u$  species, will have type-C contours with intense central branches and broad wings. Vibrations parallel to the minor or x-axis  $I_A$  (illustrated in (VIII) of Fig. 7) will according to type-A character have a less pronounced central branch and narrow wings, whereas vibrations parallel to the intermediate axis  $I_B$  will lack a central maximum between the narrow wings. As the inertial axes within the molecular plane have no special symmetry relative to bond vectors, bands of vibrations within the molecular plane, of  $B_u$  species, will in general have contours of mixed type-A and type-B character. Vibrations of  $A_g$  or  $B_g$  symmetry have no dipole transition moment, but their scattered lines in the Raman may be distinguished as the former are generally more intense and narrow, in either vapour or solid phases. With this background and the experimental data in Tables 1 and 3, we can proceed with the assignments.

For methanal- $h_2$  azine, for which data are most abundant, the fundamentals are easily assigned except  $v_7$ ,  $v_9$ ,  $v_{10}$ ,  $v_{11}$  and  $v_{12}$ ; the other fundamentals have simply been designated in Table 4 according to the format outlined above. The 614 and 413 cm<sup>-1</sup> lines observed only in Raman emission from the solid azine enable by shapes and relative intensities no unambiguous decision of  $A_{g}$  or  $B_{g}$  species. As the greater wavenumber line is the more intense, its assignment as  $\nu_7(A_g)$  is favoured leaving 413 cm<sup>-1</sup> as  $r_{12}(B_g)$ . The  $r_{10}$  and  $r_{11}$  wavenumbers have not been directly observed; the former lies beyond the accessible scan, but it would be expected to be very weak. The latter wavenumber shift presumably fails to appear in the Raman spectrum because of inherent weakness, as only two, off-diagonal, polarisability components are relevant to this mode; in support of this deduction, the other  $B_{q}$  fundamental,  $v_{12}$  assigned at 413 cm<sup>-1</sup>, is the weakest Raman line detected. However the wavenumber of  $r_{11}$  can be readily deduced from combination bands in the infrared, from both vapour and solid phase spectra. The wavenumber of  $r_{10}$  deduced from solid phase combinations is smaller than that of the torsion mode of butadiene-1,3, 161  $cm^{-1}$ , which has been directly measured in the gas phase [8]. However the greater prevalence of hot bands among the vibration-rotational bands of the azine is consistent with a small magnitude for  $v_{10}$  (vide infra). The comparatively weak solid phase absorption at 679 cm<sup>-1</sup> has been assigned as  $v_9$ ; lack of intensity in vapour phase spectra precludes detection of band type.

With regard to the wavenumbers 412, 413, 614 and 679 cm<sup>-1</sup> (solid phase), one might intuitively feel that the two pairs of similar magnitudes ought to refer to  $A_g-B_u$  and  $A_u-B_g$  pairs of related vibrations. The strongest experimental evidence against this arrangement is the lack of an intense central branch which could readily have been discerned even against the rapidly changing background due to the onset of KBr window absorption (cf. Fig. 1). As noted above, the relative intensities of 413 and 614 cm<sup>-1</sup> Raman lines also favour the apparently anomalous scheme. Moreover parallel cases persist in the repeatedly calculated butadiene-1,3 assignment [9]. Thus all the evidence, whilst not definitive, is nevertheless consistent with the assignment of Table 4.

Three additional features of the solid-phase spectra deserve comment. The

<sup>[8]</sup> G. E. CAMPAGNARO and J. L. WOOD, Trans. Faraday Soc. 62, 263 (1966).

<sup>[9]</sup> F. N. PANCHENKO, G. S. KOPTEV and V. M. TATEVSKI, Moskow Univ. Rep. (Chem.) No. 4, 49 (1969).

C.H.N.		Vibration	C, D, N,	
vapour	solid	number	vapour	solid
		A.,		
	3072 (4)	i		(2297)
	2940 ( <del>1</del> )	2	(2179)	(2168)
1615 (4)	1611 (61)	3	(1560)	(1552)
	$1427(2\frac{1}{2})$	4		(1216)
	1218 (5)	5		(1058)
	851 (41)	6	(814)	(842?)
	$614(1\frac{1}{2})$	7		
		A.,		
1019.5 (1)	1054 (3)	8	816	830
	679 (1)	9		649
	$115(1\frac{1}{2})$	10		
		B,		
(1016) (1)	(1048) (4 <del>1</del> )	11	(795)	(834)
(366) (1)	413 (2)	12		
		B <sub>u</sub>		
3078	3057 (8)	13	2310	2305
2943	2924 (4 <del>1</del> )	14	2182	2183
1637 (1)	1640 (4 <del>1</del> )	15	1580	1573
1397 (1)	1411 (3)	16	1036	1038
1166 (1)	1187 (3)	17	962	961
~380 (1)	412 (3)	18		

Table 4. Fundamentals of methanal- $h_2$  and  $-d_2$  azines

appearance, even though weak, of  $v_6$  in the absorption spectrum at 855 cm<sup>-1</sup>, is formally forbidden. However imperfections in the solid or slight distortions may give rise to weak activity. As there is no alternative assignment (apart from an *s*-cisoid rotamer), one such cause is supposed to exist. As well, two weak absorptions of the solid have been attributed to combinations of internal modes with lattice modes,  $v_{L'} + v_{11}$  at 1108 cm<sup>-1</sup> and  $v_8 + v_L$  at 1128 cm<sup>-1</sup>. As there are again no alternative assignments for these absorptions, they are presumed to arise from the azine. As only  $B_u$  combinations are present elsewhere in the spectrum, the lattice modes are tentatively deduced to be  $v_L$ ,  $B_g$ , 74 cm<sup>-1</sup> and  $v_{L'}$ ,  $A_u$ , 60 cm<sup>-1</sup>. The lattice modes considered appropriate to these wavenumbers are a translation in the *z*-direction for  $v_{L'}$  and a rotation about the *x*-axis for  $v_L$ , these being motions referred to moleculefixed axes. These assignments are speculative, at least for the time being.

In a sense, the Raman spectrum was almost superfluous, as all the wavenumbers of the Raman-active vibrations could have been—and most in fact were—deduced prior to the measurement of the Raman emission. This favourable condition arose because of the abundant, (usually) weak absorptions in the thick solid film (illustrated in part in Fig. 2), as well as a few bands in the vapour phase spectrum. Of course magnitudes deduced from these combinations are susceptible to inaccuracy of 1-30 cm<sup>-1</sup> due to anharmonicity. Direct observation leads naturally to reassurance of the correctness of the deductions, and reduces ambiguity in some cases. In Table 4, numbers in parentheses in columns beside the wavenumbers for vapour and solid phases indicate the frequency of combinations in Table 1 involving the particular fundamental. If alternative assignments of a particular combination are still possible, each fundamental involved is counted with  $\frac{1}{2}$ , rather than 1, as a weighting factor.

For methanal- $d_2$  azine, analysis can proceed in a similar manner except for two problems. First the sample from which the thick solid film of Fig. 6 was formed is suspected to be less pure than the corresponding methanal- $h_2$  azine, as the small amount of available material precluded rigorous purification. Second, isotopic impurities may absorb due to fundamental vibrations in some regions which might be confused with combinations of the fundamentals of methanal- $d_2$  azine. For these reasons we have not attempted a complete assignment of all absorptions of the solid  $C_2D_4N_2$ . However a number of likely combinations, selected in part on the prominence of parallel combinations of  $C_2H_4N_2$ , have been deduced.

Despite the paucity of data for methanal-hd azine, a number of interesting effects arise. Vibrational assignment must take into account the possible—indeed probable existence of three structural isomers [10] dependent on deuterium substitution. These are depicted by forms (V) anti-anti, (VI) syn-syn, and (VII) anti-syn, in Fig. 7. Both transoid isomers, (V) and (VI), retain  $C_{2h}$  point group. Although the anti-syn structure belongs formally to the  $C_s$  point group, additional vibrational modes made formally active in absorption according to the decrease of symmetry will have only slight intensity as electronic structure is perturbed almost negligibly by isotopic substitution. Since there is no precedent for a strong isotopic effect to operate during synthesis of the azines, all of the forms (V), (VI) and (VII) are approximately equally probable. Therefore one might expect up to three sets of bands in any region for a particular group vibration. However only for vibrations consisting of considerable hydrogen motion might distinctly separate bands appear.

Considering the spectrum of Fig. 4, we find in the  $3000 \text{ cm}^{-1}$  region two wellformed bands centred at 2990 and  $3059 \text{ cm}^{-1}$ , with strong indication of a further, weaker band near 2940 cm<sup>-1</sup>. Again near 2250 cm<sup>-1</sup>, two well-formed bands are centred at 2218 and 2269 cm<sup>-1</sup>, but any potential third band is effectively masked. There is only one band at 1608 cm<sup>-1</sup>, appropriate to the antisymmetric C==N stretching vibration, with a related single band at 3170 cm<sup>-1</sup> as will be explained later.



Fig. 8. Infra-red absorption between 1080–880 cm<sup>-1</sup>, of  $C_2H_2D_2N_2$  vapour. Pressure and cell as in Fig. 3. Spectral slit width ~0.8 cm<sup>-1</sup>.

<sup>[10]</sup> E. ARNAL, J. ELGUERO, R. JACQUIER, C. MARZIN and J. WYLDE, Bull. Soc. Chim. France 877 (1965).

There is only one poorly formed band at  $1305 \text{ cm}^{-1}$ , presumably resulting from a superposition of HCD-scissoring modes for the various structural isomers. Near  $950 \text{ cm}^{-1}$  a complex band appears with three distinct prominent features. Abscissa expansion with better resolution, as in Fig. 8, shows the features at 952 and 965 cm<sup>-1</sup> each to resemble the central regions of the 1017 [Fig. 9(b)] and 816 cm<sup>-1</sup> (Fig. 10) bands of  $C_2H_4N_2$  and  $C_2D_4N_2$  respectively. However the third main feature about 938 cm<sup>-1</sup> has a different pattern; this feature might conceivably arise from either a fortuitous superposition of  ${}^{p}Q$  band heads from the other two main bands, or a central branch of a third main band. The irregular spacing and intensity behaviour is taken to favour the latter alternative. In that case, definite evidence of the existence of three distinct structural isomers is here provided. An additional band, one of the two—neither well-formed—at 1853 and 1903 cm<sup>-1</sup>, is presumably due to combinations of the symmetric and antisymmetric wagging domes as at 2033 and 1615  $\text{cm}^{-1}$  of  $C_2H_4N_2$  and  $C_2D_4N_2$  respectively. There is no indication of bands for the methylene rocking vibrations which should have wavenumbers between 1000 and  $1150 \text{ cm}^{-1}$ : although the boundaries of this interval do contain absorption due to other bands. if the sought bands had relative intensity comparable to the 1166 and 962  $cm^{-1}$ counterparts for  $C_2H_4N_2$  and  $C_2D_4N_2$  respectively, they should have been detected.

One clear conclusion which we can draw on the basis of the vibration wavenumbers concerns bands in the region of  $3200 \text{ cm}^{-1}$ . Owing to its position and intensity, the  $3235 \text{ cm}^{-1}$  band was earlier [2] considered to be a C—H stretching mode fundamental—it is in fact considerably more intense than the fundamental at 1637 cm<sup>-1</sup>. However, the small displacement, from 3235 through 3170 to 3140cm<sup>-1</sup> for  $C_2H_4N_2$ ,  $C_2H_2D_2N_2$  and  $C_2D_4N_2$  respectively, proves that the mode involves only slight hydrogen motion. The decrease in fact closely parallels the decrease, from 1637 through 1608 to  $1581 \text{ cm}^{-1}$ , of the C—N mode, so that there can be no doubt of the correctness of the revised assignment as combinations of corresponding infra-red and Raman-active C—N stretching fundamentals. Doubtless Fermi resonance causes some enhancement of the  $3235 \text{ cm}^{-1}$  band, but even for the rather small sample of  $C_2D_4N_2$  the band at  $3140 \text{ cm}^{-1}$  is still plainly visible. A somewhat similar case for the combination of wagging modes at 2033, 1853, 1615 cm<sup>-1</sup> applies in that in all three instances the intensities are remarkably great.

There are several aspects of this vibrational assignment which could benefit from a normal coordinate analysis. In fact, assignments must be regarded as both qualitative and tentative until tested by a thorough computation. Attribution of specific absorptions to the various structural isomers of methanal-hd azine, confirmation of tentative assignment of some of the smaller wave-number bands of methanal- $h_2$ azine, and prediction of active combinations for methanal- $d_2$  azine might fruitfully result from such a procedure. As well of course, harmonic force field parameters and potential energy distribution can also be calculated. This information is valuable in its own right, as well as for comparison with related conjugated molecules like butadiene-1,3. These computations are under way.

### Vapour phase spectroscopic effects

Most absorption bands of each isotopic methanal azine vapour show a welldefined contour with distinct P- and R- branches, and in some cases central branches



Fig. 9. Infra-red absorption between (a) 1240–1120, (b) 1050–980 and (c) 3000–2900 cm<sup>-1</sup> of  $C_2H_4N_2$  vapour, ~5 hN m<sup>-2</sup> pressure; path length 2.5–6.25 m. Spectral slit width 0.2–0.3 cm<sup>-1</sup>. Ordinate is percent transmittance, and abscissa is wavenumber in cm<sup>-1</sup>.



Fig. 10. Infra-red absorption between  $1000-760 \text{ cm}^{-1}$  of  $C_2D_4N_2$  vapour. Pressure and cell as in Fig. 5. Spectral slit width  $\sim 0.7 \text{ cm}^{-1}$ .

as well. A few bands show in addition resolvable fine structure in the various branches. For  $v_8$  of  $C_2H_4N_2$ , the fine structure under comparatively poor resolution (0.7 cm<sup>-1</sup>) was analysed after tentative numbering of the outer sequences of peaks. Obtained by the method of combination sum and differences, the results are:  $v_0 = 1019.5 \pm 0.2$  cm<sup>-1</sup>, and apparent rotational constants (A-B) for lower and upper states,  $1.51 \pm 0.01$  and  $1.48 \pm 0.01$  cm<sup>-1</sup> respectively. The corresponding results for  $v_8$  of  $C_2D_4N_2$  under similar resolution are  $v_0 = 816.6 \pm 0.2$  cm<sup>-1</sup>, and apparent rotational constants for lower and upper states, 1.13  $\pm$  0.015 and 1.11  $\pm$ 0.015 cm<sup>-1</sup> respectively. The corresponding quantities for  $v_{10}$  of butadiene-1,3- $h_6$ under similar resolution [11] are  $v_0 = 908.8$  cm<sup>-1</sup> and lower and upper state constants, 1.23 and 1.20 cm<sup>-1</sup>. Comparison of the similarity of the general form of the bands and the magnitudes of the rotational constants leaves no doubt that butadiene-1,3 and methanal azine have similar conformations and structures. Corroboration is afforded by a calculation, using reasonable trial structural parameters, of effective rotational constants for various conformations: for the s-cisoid structure (I),  $0.52 \text{ cm}^{-1}$ , and for the s-transoid structure, (II),  $1.45 \text{ cm}^{-1}$ . Also for comparison, the effective rotational constant of N-methylene diazirine (IV) can be expected to resemble that of methylenecuclopropane for which an effective rotational constant  $0.44 \text{ cm}^{-1}$ can be derived from experimental rotational constants [12]. Thus the gross equilibrium conformation of the prevalent form of methanal azine has finally been definitively established.

Rotational analysis of some bands measured under better resolution was attempted. The magnitude of Ray's assymmetry parameter,  $\kappa = -0.98$  based on reasonable trial structural parameters for the s-transoid conformation, indicates by its proximity to -1.0 that methanal- $h_2$  azine is an only slightly asymmetric rotor, for which prolate

<sup>[11]</sup> D. J. MARAIS, N. SHEPPARD and B. P. STOICHEFF, Tetrahedron 17, 163 (1962).

<sup>[12]</sup> V. W. LAURIE and W. M. STIGLIANI, J. Am. Chem. Soc. 92, 1485 (1970).

symmetric rotor formulae constitute good approximations. There are three types of vibration-rotational bands of asymmetric rotors [13]. Type-A bands show a weak but narrow central branch of unresolved Q-lines ( $\Delta J = 0$ ,  $\Delta K = 0$ ), with relatively narrow R- and P- branches ( $\Delta J = \pm 1$ ,  $\Delta K = 0$ ) also of unresolved lines, such as  $v_{14}$  of  $C_2H_4N_2$  in Fig. 9(c). Type-B bands resemble type-A except that they lack a central Q-branch ( $\Delta J = 0$ ,  $\Delta K = 0$ ) and have in addition more or less prominent sequences of Q-branches ( $\Delta J = 0$ ,  $\Delta K = \pm 1$ ) on the wings, such as  $v_{17}$  of  $C_2H_4N_2$  in Fig. 9(a). Actually, as explained earlier, mixed A/B type is to be expected for all vibrations within the molecular plane (i.e. of  $B_u$  species); however it may happen that transition moments for particular vibrations have directions which almost coincide with the minor or intermediate inertial axes, in which case the  ${}^{p}Q$ - and  ${}^{r}Q$ - branches are either very weak or much stronger respectively, with a central  ${}^{q}$ -branch correspondingly strong or apparently absent. Type-C bands have intense central Q-branches and broad wings with very prominent  ${}^{p}Q$ - and  ${}^{r}Q$ - heads and underlying structure, such as  $v_8$  of  $C_2H_4N_2$  in Fig. 9(b).

Some bands of  $C_2H_4N_2$  under resolution of  $\sim 0.2 \text{ cm}^{-1}$  yielded the results in Table 5 after analysis by application of combination relations. Despite the internal consistency of data for each band, as indicated by relatively small values of standard

Vibration number	ν <sub>0</sub>	$(A'' - \tilde{B}'')$	$(A'-\bar{B}')$	(A' - B') - (A'' - B'')
8	$1019.5 \pm 0.03$	$1.464 \pm 0.006$	$1.429 \pm 0.004$	$-0.0272 \pm 0.0005$
16	$1397.3 \pm 0.3$	$1.520 \pm 0.015$	$1.523 \pm 0.015$	$+0.0028 \pm 0.0016$
17	$1166.1 \pm 0.07$	$1.440 \pm 0.005$	$1.451 \pm 0.004$	$+0.0167 \pm 0.0006$

Table 5. Results of rotational analyses on bands of  $C_2H_4N_2$ 

deviations, the ground state rotational constants for the different bands agree poorly. No reasonable adjustment of rotational numbering produced better results. The major causes of the discrepancies are the interference by lines of superimposed bands of molecules in vibrationally excited lower states ("hot bands"), and non-linearity of wavenumber scan on the spectrometer used.

Notwithstanding these handicaps, we can draw some useful deductions from the results of the analyses. The quantity (A' - B') - (A'' - B''), obtained from the combination sum relation

$${}^{r}Q(K) + {}^{p}Q(K) = 2[r_{0} + (A' - \bar{B}')] + 2[(A' - \bar{B}') - (A'' - \bar{B}'')]K^{2},$$

has much greater absolute accuracy than the rotational constants (A - B) themselves. Also tests of the spectrometer with bands of HCN and DCN indicate that, although the rotational constants for both upper and lower states are slightly inaccurate, the deviations are similar for both rotational constants B' and B'' of a given band in most regions of the accessible scanning range. Therefore useful information can be derived from the slopes of graphs of  ${}^{r}Q(K) + {}^{p}Q(K)$  vs.  $K^{2}$ , even though the

<sup>[13]</sup> H. C. ALLEN and P. C. CROSS, Molecular Vib-Rotors. John Wiley (1963).

absolute accuracy of the rotational constants is inadequate for many purposes. The quantity  $(A' - \bar{B}') - (A'' - \bar{B}'')$  contains or hides contributions from various sources, for instance, change of individual rotational constant (A, B or C) with vibrational state, and centrifugal distortional effects which are not allowed for elsewhere. Neglecting the latter, the main contribution is expected to be an  $\alpha$ -value. For these prolate rotors,  $A \ge B \sim C$ , and the largest contribution to  $\alpha$  is probably associated with the *change* in A. On comparison of the three values of  $(A' - \bar{B}') - (A'' - \bar{B}'')$  reported in Table 5, we find one reasonably small value, and two others for adjacent bands which are of much larger magnitude but opposite sign. The last feature suggests some vibration-rotational interaction [14], and further evidence confirms in fact that a Coriolis coupling of  $\nu_8$  and  $\nu_{17}$  occurs for both  $C_2H_4N_2$  and  $C_2D_4N_2$ .

The usual features of a Coriolis interaction are well illustrated in the absorption of  $C_2D_4N_2$  shown in Fig. 10. The vibrational modes which interact have similar wavenumbers, in this case 816 and  $962 \text{ cm}^{-1}$ . Effects are seen in both intensity anomalies and rotational spacing. In this case, the R-branch of  $r_{17}$ , the weaker band, is much more intense than the P-branch, whereas the reverse is true for  $r_{e}$ but to a lesser extent. The resolvable fine structure, the Q-head sequences, tend to converge in the  $^{p}Q$ -branch of  $r_{17}$  and the  $^{r}Q$ -branch of  $r_{8}$ . The latter effect is of course manifest in the apparent  $\alpha$ -values. The Coriolis interaction probably accounts for 75-90% of the magnitude of  $(A' - \bar{B}') - (A'' - \bar{B}'')$  for these two bands, as substantiated by the much smaller magnitude of this parameter for  $r_{16}$ . According to Jahn's rule, Coriolis coupling can occur between two vibrational modes if the direct product of the symmetry species of the vibrations transforms like a molecular rotation. In the case of  $C_{2h}$  molecules, a vibration of species  $A_{u}$  can interact with a vibration of species  $B_u$ , as the direct product  $B_q$  transforms like a rotation about axes in the plane perpendicular to the figure axis. However for asymmetric rotor molecules, what the point group table says about the symmetry species of  $R_x$ ,  $R_y$ ,  $R_z$  is effectively irrelevant, as there are six ways of orienting the spatial axes with the inertial axes. Coriolis interaction about the z-axis of a symmetric rotor affects the K-structure, whereas this interaction about the x- and y-axes affects the J- structure thereby failing to produce observable effects in these large molecules. In the acyclic azines, the interaction will produce effects observable in the rotational constants if the molecular rotation concerned in the direct product is about an axis almost coincident with the principal axis of least moment of inertia. This axis of least inertial moment would in fact be the z-axis or figure axis of the rotor in the prolate symmetric limit. The forms of the vibrations belonging to  $r_8$  (transition moment necessarily along the z-axis or  $I_{C}$ ) and  $v_{17}$  (transition moment nearly along the y-axis or  $I_{B}$ , as indicated in (VIII) in Fig. 7) indicate that this explanation is appropriate. (This rotational evidence further corroborates the vibrational assignment earlier presented). Finally the closer are the centres of the bands of the interacting modes, the stronger is the coupling. Thus the two fundamentals  $r_8$  at 1019 cm<sup>-1</sup> and  $r_{17}$  at 1166 cm<sup>-1</sup> make Coriolis coupling most favourable for detection in methanal- $h_2$  azine. Also it is worth noting that in the limit of a prolate symmetric rotor,  $v_8$  and  $v_{17}$  become components of a degenerate bending mode.

<sup>[14]</sup> I. M. MILLS, Pure Appl. Chem. 11, 325 (1965).

Again attempts to treat quantitatively the Coriolis interaction in the spectra of  $C_2H_4N_2$ , obtained under the best available resolution, were hampered by the overlapping "hot" bands and non-linear scan. However, by the method of SMITH and MILLS [15], we have derived an approximate magnitude for  $A\zeta = 0.80 \pm 0.02$ . To evaluate  $\zeta_{i}$ , we require a value for the rotational constant A. The average separation of the maxima of the P- and R-branches of bands at 1640, 2945, 3080 and 3235  $cm^{-1}$  of  $C_{2}H_{4}N_{2}$  is 20.4  $\pm$  0.25 cm<sup>-1</sup>. Under the assumptions of a rigid planar rotor  $(C^{-1} = A^{-1} + B^{-1})$  and negligible change in rotational constants in the vibrational states involved ( $v_8 = 1$ ,  $v_{17} = 1$ , and the ground state), we have calculated, by the method of SETH PAUL and DIJKSTRA [16], that for  $A = \frac{1}{2}(B+C) = 1.44$ , A = 1.64and (B+C)/2 = 0.195 cm<sup>-1</sup>. Hence  $|\zeta_{8,17}| = 0.49$ , with an error estimated as  $\pm 0.05$ . For the reasons outlined above, an alternative description as a z-axis Coriolis interaction may be preferable, i.e.  $|\zeta_{8,17}^z|$ , particularly for comparison with related molecules. The Coriolis constants for coupling between corresponding methylene vibrations are for ethene [15],  $0.44 \pm 0.02$ , propadiene [17], 0.53 and 0.56, methanal [18], 0.54, and butadiene-1,3 [19], 0.46  $\pm$  0.03. For C<sub>2</sub>D<sub>4</sub>N<sub>2</sub>,  $|\zeta_{8,17}^z|$  can be estimated [19] to be roughly 0.7.

Finally we comment on the complicated structure of the vibration-rotational bands of the azines. In each case of  $r_8$ , 1019 cm<sup>-1</sup> for  $C_2H_3N_2$ , 817 cm<sup>-1</sup> for  $C_2D_4N_2$ , and at least 952 and 965 cm<sup>-1</sup> for  $C_2H_2D_2N_2$ , these are three intense line-like features where only one is expected at the band centre. These are attributed to  $^{o}Q$ -branches  $(\Delta J = \Delta K = 0)$  of bands originating in vibrationally excited states. As already mentioned, the value of  $v_{10} = 115 \text{ cm}^{-1}$ , deduced from solid-phase combinations, is markedly smaller than that of the butadiene-1,3 torsional mode [8], 161 cm<sup>-1</sup>. The distinct separation of Q-branches of 'hot' bands, and their consequent extension over a greater wavenumber range, means that the torsional vibration of  $C_2H_4N_2$ is more anharmonic than for butadiene-1,3. The energy levels can be estimated to be  $v_{10} = 115, 2v_{10} = 227.8$  and  $3v_{10} = 340.7$  cm<sup>-1</sup>. The appropriate Boltzmann factors are 0.58, 0.34 and 0.20 respectively. The wavenumber of  $v_{10} = 3$  is still smaller than that for any other fundamental, according to Table 4. In the case of butadiene-1,3 [20], three extra sets of  ${}^{p}Q$ - and  ${}^{r}Q$ -branches were found to be associated with the main band at  $908 \text{ cm}^{-1}$ ; in that case only a single broad central branch can be observed, but the satellite  ${}^{p}Q$ - and  ${}^{r}Q$ -lines were sufficiently separated to be measured and analysed. This procedure was not possible for our azine spectra. As well, further structure around the centre of  $v_{s}$ , in Fig. 9(b) may require explanation other than "hot" bands.

Both accurate determination of structural parameters and quantitative treatment of Coriolis interactions must await acquisition of spectra of substantially improved resolution.

<sup>[15]</sup> W. L. SMITH and I. M. MILLS, J. Chem. Phys. 40, 2095 (1964).

<sup>[16]</sup> W. A. SETH PAUL and G. DIJKSTRA, Spectrochim. Acta 23A, 2861 (1967).

<sup>[17]</sup> I. M. MILLS, W. L. SMITH and J. L. DUNCAN, J. Mol. Spectry 16, 349 (1965).

<sup>[18]</sup> H. H. BLAU and H. H. NEILSEN, J. Mol. Spectry 1, 124 (1957).

<sup>[19]</sup> J. F. OGILVIE and K. C. COLE, J. Mol. Spectry, 35 332 (1970).

<sup>[20]</sup> A. R. H. COLE, G. M. MOHAY and G. A. OSBORNE, Spectrochim. Acta 23A, 909 (1967).

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