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of Astrophysical Interest

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## SUMMARY OF PROGRESS

Gerard P. Kuiper<sup>1</sup> has pointed out that the Jovian atmospheres are expected to contain  $H_2$ , He,  $N_2$ ,  $H_2O$ ,  $NH_3$ ,  $CH_4$ , Ar and possibly  $SiH_4$ . He has also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below  $120^\circ C$  [see Table 8, pg. 349-350 of reference (1)]. He has also pointed out that until more is known about the atmospheres of the planets, it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work.

We have been studying the vibrational spectra from  $4000$  to  $33\text{ cm}^{-1}$  of several molecules which may be present in the atmosphere of the Jovian planets. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the compositions of the cloud covers of several of the planets; (2) provide structural information under favorable circumstances; (3) provide necessary data from which accurate thermodynamic data can be calculated; (4) and furnish information as to the nature of the potential energy function of the molecules and forces acting within them.

Some of the molecules which we have studied can be produced photochemically from methane, ammonia, and hydrogen sulfide which are thought to be constituents of the planets with reducing atmospheres. Some of the compounds will polymerize under ultraviolet radiation and drop out of the atmospheres. However, planets with a hot base, like that of Jupiter, may rebuild molecules destroyed photochemically. Therefore, we have used these criteria in selecting the compounds which we have studied. In our initial work on the vibrational spectra of molecules of astrophysical interest we studied hydrazine<sup>2</sup> and methylamine.<sup>3</sup> However, there are several other small molecules which contain hydrogen, carbon and nitrogen which also should be possible constituents of the reducing atmospheres and we previously selected methylhydrazine<sup>4</sup>, unsymmetrical dimethylhydrazine<sup>5</sup>, symmetrical dimethylhydrazine<sup>6</sup>, propylene imine<sup>7</sup>, 1-pyrazoline<sup>8</sup>, and HNCS and

DNCS.<sup>9</sup> In our continued study of nitrogen containing compounds, we have completed our work on azomethane and azomethane-d<sub>6</sub>. A copy of the paper on this study as submitted to the Journal of Chemical Physics can be found in Appendix I.

Closely related to these nitrogen containing compounds has been our work on the carbonyl containing molecules. We have previously reported work on carbon trioxide<sup>10</sup>, trifluoromethyl peroxide<sup>11</sup>, ethylene carbonate<sup>12</sup>,  $\gamma$ -butyrolactone<sup>12</sup>, cyclopentanone<sup>12</sup>, oxalyl chloride<sup>13</sup>, glyoxal<sup>14</sup>, oxalyl bromide<sup>15</sup>, oxalyl fluoride<sup>16</sup>, 2,3 butanedione<sup>17</sup> (biacetyl), thiooxamide<sup>18</sup> and oxamide<sup>18</sup>. We have not concluded any further work in this area during this reporting period; however, studies are in progress on oxalylchlorofluoride and oxamic acid.

In a previous far infrared study<sup>19</sup>, we analyzed the spectrum of the ring-puckering vibration of 1-pyrazoline and determined that the barrier to the planar conformation was 113 cm<sup>-1</sup> by using a potential function of the form:<sup>20</sup>

$$V = A_s X^4 + (B_s - D_t + H_t) X^2. \quad (1)$$

The  $A_s$  and  $B_s$  coefficients result from the angle strain, whereas the  $D_t$  and  $H_t$  terms represent the torsional repulsions. The magnitude of the inversion barrier in 1-pyrazoline (113 cm<sup>-1</sup>) was compared in a qualitative fashion with the 232 cm<sup>-1</sup> barrier previously determined for cyclopentene.<sup>21</sup> By assuming that the torsional forces in the two rings were comparable, the barrier height difference was attributed to an increase in angle strain at the  $\alpha$ -positions of 1-pyrazoline. It should be noted that it is the ring strain which tends to make the ring planar and the puckering results so that the torsional interactions are minimized.

There is little doubt that the  $D_t$  term is essentially the same for both 1-pyrazoline and cyclopentene since it represents the CH<sub>2</sub>-CH<sub>2</sub> torsional force. The  $H_t$  term, however, results from the torsional force about the CH<sub>2</sub>-X bond (where X = N for 1-pyrazoline and X = C for cyclopentene) and may differ for each ring. One should be able to deduce the relative magnitude of  $H_t$  in the

respective cyclic systems by correlating it with the torsional barriers in analogous open chain molecules. For example, the methyl torsional barrier in propylene should permit a reasonable estimate of  $H_t$  for cyclopentene, whereas the barrier in azomethane will provide similar information for 1-pyrazoline. Microwave investigations of propylene<sup>22</sup> have shown that the  $\text{CH}_3$  rotational barrier is 1.98 kcal/mole; however, there is no published data relating to the torsional barrier in azomethane. For this reason, the present study of  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  was initiated.

There have been two previous vibrational studies of azomethane<sup>23,24</sup> but these are quite incomplete and there was no mention of the interesting torsional vibrations. Additionally, the earlier investigations were made without the benefit of isotopic substitution; consequently, there is some uncertainty in the proposed vibrational assignments. For example, West and Killingsworth<sup>23</sup> suggest that a Raman line at  $1442\text{ cm}^{-1}$  results from the  $\text{N}=\text{N}$  stretching motion rather than a  $\text{CH}_3$  deformational mode. Such a description does not appear to be consistent with what is now known about the  $\text{N}=\text{N}$  moiety<sup>1</sup> since the "group frequency" appears to be  $1555 \pm 30\text{ cm}^{-1}$ . A definitive assignment of this vibration should be possible by simultaneously studying the spectrum of  $\text{CD}_3\text{NNCD}_3$ . Dipole moment and electron diffraction studies<sup>25,26</sup> indicate that the methyl groups in azomethane are trans and the earlier vibrational data suggests mutual exclusion.

The infrared and Raman spectra of  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  have been examined in detail. A vibrational assignment is suggested for the 24 fundamental modes which is consistent with the molecule having  $\text{C}_{2h}$  symmetry. The spectra on the polycrystalline samples provide evidence that there are at least four molecules per unit cell since a number of the bands were observed to be split into doublets. The crystal also appears to have a center of symmetry since mutual exclusion is clearly operative. The  $b_g$  and  $a_u$  torsional fundamentals were observed at 223 and  $222\text{ cm}^{-1}$ , respectively, for the normal molecule. From the  $1 \leftarrow 0$  frequencies

of the  $a_u$  torsion in solid  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  internal rotational barriers of 2.69 and 2.60 kcal/mole were calculated, respectively. The Thermodynamic properties have been calculated for gaseous  $\text{CH}_3\text{NNCH}_3$  and are presented in Table 1.

Future Work (NGR-41-002-033)

We are continuing our investigation of the vibrational spectra of small molecules which may be possible constituents of the Jovian atmospheres. The data will be used to calculate thermodynamic properties, force constants, and other useful molecular properties when possible. At present work is continuing on oxalylchlorofluoride and oxamic acid in our study of molecules containing carbonyl. Work is also progressing on dimethylphosphine and dimethylamine, both of which fits the criteria as a possible constituent of the Jovian atmospheres. We have also initiated studies on nitric oxide dimer ( $N_2O_2$ ) and perfluoro-nitrosomethane ( $CF_3NO$ ) which also satisfy this criteria.

## REFERENCES

1. G. P. Kuiper, Atmospheres of the Earth and Planets. University of Chicago, Chicago Press, Chicago, 1952.
2. J. R. Durig, S. F. Bush, and E. E. Mercer, J. Chem. Phys., **44**, 4238 (1966).
3. J. R. Durig, S. F. Bush, and F. G. Baglin, J. Chem. Phys., **49**, 2106 (1968).
4. J. R. Durig, W. C. Harris, and D. W. Wertz, J. Chem. Phys., **50**, 1449 (1969)
5. J. R. Durig and W. C. Harris, J. Chem. Phys., **51**, 4457 (1969).
6. J. R. Durig and W. C. Harris, J. Chem. Phys., **54**, 0000 (1971).
7. J. R. Durig, S. F. Bush, and W. C. Harris, J. Chem. Phys., **50**, 2851 (1969).
8. J. R. Durig, J. M. Karriker, and W. C. Harris, J. Chem. Phys., **52**, 6096 (1970).
9. J. R. Durig, C. M. Player, Jr., J. Bragin, and W. C. Harris, Mol. Cryst. Liq. Cryst., in press.
10. J. R. Durig and G. Nagarajan, Monatshefte für Chemie, **99**, 473 (1968).
11. J. R. Durig and D. W. Wertz, J. Mol. Spectry., **25**, 467 (1968).
12. J. R. Durig, G. L. Coulter, and D. W. Wertz, J. Mol. Spectry., **27**, 285 (1968).
13. J. R. Durig and S. E. Hannum, J. Chem. Phys., **52**, 6089 (1970).
14. J. R. Durig and S. E. Hannum, J. Crystal Mol. Struct., **1**, 131 (1971).
15. J. R. Durig, S. E. Hannum, and F. G. Baglin, J. Chem. Phys., in press.
16. J. R. Durig, S. C. Brown, and S. E. Hannum, J. Chem. Phys., **54**, 0000 (1971).
17. J. R. Durig, S. E. Hannum, and S. C. Brown, J. Phys., Chem., in press.
18. J. R. Durig, S. C. Brown, and S. E. Hannum, Mol. Cryst. Liq. Cryst., in press.
19. J. R. Durig, J. M. Karriker, and W. C. Harris, J. Chem. Phys., **52**, 6096 (1970).
20. J. Laane, J. Chem. Phys., **50**, 776 (1969).
21. J. Laane and R. C. Lord, J. Chem. Phys., **47**, 4941 (1967).
22. D. R. Lide and D. E. Mann, J. Chem. Phys., **27**, 868 (1957).
23. W. West and R. B. Killingsworth, J. Chem. Phys., **6**, 1 (1938).
24. L. Kohovec and K. W. F. Kohlrausch, Z. Physik Chem., **B38**, 96 (1937).
25. A. Almennigen, I. M. Anfinsen, and A. Haaland, Acta. Chem. Scand., **24**, 1230 (1970).
26. H. Boersch, Monatsch., **65**, 311 (1935).

Table 1  
Thermodynamic Calculations for Azomethane\*

	S	$-(F-H_0)/T$	$(H-H_0)/T$	Cp
Temperature = 298.150°K				
Translational	38.093476	33.125551	4.967925	4.967925
Rotational	22.202630	19.222880	2.979750	2.980755
Vibrational	3.690686	1.191163	2.499523	6.843150
Total & Internal Rotation	69.801660	56.319998	13.480492	19.262215
Temperature = 400.000°K				
Translational	39.553389	34.585464	4.967925	4.967925
Rotational	23.098572	20.098572	2.980006	2.980755
Vibrational	6.274002	2.146672	4.127329	10.990044
Total & Internal Rotation	76.019464	60.558517	15.459778	23.210729
Temperature = 500.000°K				
Translational	40.661950	35.694025	4.967925	4.967925
Rotational	23.743714	20.763558	2.980155	2.980755
Vibrational	9.161831	3.256785	5.905046	14.982991
Total & Internal Rotation	81.597353	64.219871	17.37614	26.845160
Temperature = 600.000°K				
Translational	41.567709	36.599784	4.967925	4.967925
Rotational	24.287170	21.306914	2.980255	2.980755
Vibrational	12.214797	4.494108	7.720690	18.532801
Total & Internal Rotation	86.779879	67.556201	19.222508	30.052406
Temperature = 700.000°K				
Translational	42.333519	37.365593	4.967925	4.967925
Rotational	24.746655	21.766328	2.980327	2.980755
Vibrational	15.308115	5.818053	9.490062	21.603715
Total & Internal Rotation	91.625698	70.648642	20.975888	32.844702

Table 1. (continued)

## Thermodynamic Calculations for Azomethane\*

	S	-(F-H <sub>o</sub> )/T	(H-H <sub>o</sub> )/T	C <sub>p</sub>
Temperature = 800.000°K				
Translational	42.996892	38.028967	4.967925	4.967925
Rotational	25.144680	22.164299	2.980380	2.980755
Vibrational	18.370001	7.196256	11.173745	24.249779
Total & Internal Rotation	96.170902	73.563960	22.605773	35.262694
Temperature = 900.000°K				
Translational	43.582029	38.614104	4.967925	4.967925
Rotational	25.495762	22.515340	2.980422	2.980755
Vibrational	21.361244	8.604737	12.756508	26.531238
Total & Internal Rotation	100.454852	76.308249	24.145432	37.365777
Temperature = 1000.000°K				
Translational	44.105453	39.137527	4.967925	4.967925
Rotational	25.809816	22.829360	2.980455	2.980755
Vibrational	24.261008	10.026193	14.234815	28.499582
Total & Internal Rotation	104.481505	78.936133	25.544660	39.199986

\*These calculations were made using gas phase frequencies and assuming all vibrations to be harmonic except the methyl torsions. Assuming the following molecular geometry:  $r(\text{N}=\overset{\circ}{\text{N}}) = 1.247\text{\AA}$ ,  $r(\text{C}-\overset{\circ}{\text{N}}) = 1.482\text{\AA}$ ,  $r(\text{C}-\overset{\circ}{\text{H}}) = 1.105\text{\AA}$ , and  $\angle \text{CNN} = 112.3^\circ$ ; the moments of inertia  $I_A = 121.5$ ,  $I_B = 115.7$ ,  $I_C = 12.3$  and  $I_{\text{red}} = 2.51 (\text{AMU})\text{\AA}^2$  were calculated and used in these calculations presented.

## Appendix I

### Vibrational Spectra and Structure of Azomethane and Azomethane-d<sub>6</sub>

ABSTRACT: The infrared spectra of gaseous and polycrystalline  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  have been recorded from 33 to  $4000\text{ cm}^{-1}$ . The corresponding Raman spectra of the liquid and solid samples have been measured from 100 to  $4000\text{ cm}^{-1}$ . The vibrational data provide definitive verification of a trans structure with  $\text{C}_{2h}$  symmetry. A vibrational assignment is proposed for the 24 fundamental modes based upon the observed band contours, isotopic shift ratios, and group frequency correlations. The  $a_u$  and  $b_g$  torsional modes were assigned to bands at 222 and  $223\text{ cm}^{-1}$ , respectively, and the internal rotational barrier of the methyl group was calculated to be approximately 2.7 kcal/mole. A number of the internal fundamentals were observed to be split into doublets in the spectra of the solids which suggests that there are at least four molecules per unit cell in azomethane. The inversion center is apparently retained in the crystal since the rule of mutual exclusion was found to be operative.

## INTRODUCTION

In a previous far infrared study<sup>1</sup>, we analyzed the spectrum of the ring-puckering vibration of 1-pyrazoline and determined that the barrier to the planar conformation was  $113 \text{ cm}^{-1}$  by using a potential function of the form<sup>2</sup>:

$$V = A_s \chi^4 + (B_s - D_t + H_t) \chi^2. \quad (1)$$

The  $A_s$  and  $B_s$  coefficients result from the angle strain, whereas the  $D_t$  and  $H_t$  terms represent the torsional repulsions. The magnitude of the inversion barrier in 1-pyrazoline ( $113 \text{ cm}^{-1}$ ) was compared in a qualitative fashion with the  $232 \text{ cm}^{-1}$  barrier previously determined for cyclopentene<sup>3</sup>. By assuming that the torsional forces in the two rings were comparable, the barrier height difference was attributed to an increase in angle strain at the  $\alpha$ -positions of 1-pyrazoline. It should be noted that it is the ring strain which tends to make the ring planar and the puckering results so that the torsional interactions are minimized.

There is little doubt that the  $D_t$  term is essentially the same for both 1-pyrazoline and cyclopentene since it represents the  $\text{CH}_2\text{-CH}_2$  torsional force. The  $H_t$  term, however, results from the torsional force about the  $\text{CH}_2\text{-X}$  bond (where  $X=\text{N}$  for 1-pyrazoline and  $X=\text{C}$  for cyclopentene) and may differ for each ring. One should be able to deduce the relative magnitude of  $H_t$  in the respective cyclic systems by correlating it with the torsional barriers in analogous open chain molecules. For example, the methyl torsional barrier in propylene should permit a reasonable estimate of  $H_t$  for cyclopentene, whereas the barrier in azomethane will provide similar information for 1-pyrazoline. Microwave investigations of propylene<sup>4</sup> have shown that the  $\text{CH}_3$  rotational barrier is  $1.98 \text{ kcal/mole}$ ; however, there is no

published data relating to the torsional barrier in azomethane. For this reason, the present study of  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  was initiated.

There have been two previous vibrational studies of azomethane<sup>5,6</sup>, but these are quite incomplete and there was no mention of the interesting torsional vibrations. Additionally, the earlier investigations were made without the benefit of isotopic substitution; consequently, there is some uncertainty in the proposed vibrational assignments. For example, West and Killingsworth<sup>5</sup> suggest that a Raman line at  $1442\text{ cm}^{-1}$  results from the N=N stretching motion rather than a  $\text{CH}_3$  deformational mode. Such a description does not appear to be consistent with what is now known about the N=N moiety<sup>1</sup> since the "group frequency" appears to be  $1555 \pm 30\text{ cm}^{-1}$ . A definitive assignment of this vibration should be possible by simultaneously studying the spectrum of  $\text{CD}_3\text{NNCD}_3$ . Dipole moment and electron diffraction studies<sup>7,8</sup> indicate that the methyl groups in azomethane are trans and the earlier vibrational data suggests mutual exclusion.

#### EXPERIMENTAL

The samples of  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  were obtained commercially (Merck, Sharp, and Dohme of Canada, Ltd., Montreal, Canada), and purified by trap-to-trap vacuum distillation. The main contaminate was  $\text{CO}_2$  and the purification was followed by the relative intensity of the infrared band at  $672\text{ cm}^{-1}$ .

The mid-infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer. The instrument housing was purged with dry

air to remove atmospheric water vapor. The spectrophotometer was calibrated by using standard gases in the higher-frequency region<sup>9</sup> whereas the lower-frequency region<sup>10</sup> was calibrated with atmospheric water vapor. A 20 cm cell equipped with CsI windows was utilized to record the spectra of the gaseous samples (see Fig. 1). The spectra of the polycrystalline samples were obtained by slowly subliming the compounds onto a CsI support maintained at liquid nitrogen temperature (see Fig. 2).

The far-infrared spectra were recorded on a Beckman IR-11 infrared spectrophotometer from 33 to 500  $\text{cm}^{-1}$  and the instrument was calibrated with water vapor bands<sup>10</sup>. A 10 m multipath cell equipped with polyethylene windows was employed in the study of the gaseous samples, whereas a cold cell which utilized a silicon support was used in the study of the solid materials (see Fig. 3). The silicon plate was maintained at liquid nitrogen temperature and the samples were repeatedly annealed.

The Raman spectra were recorded on a Cary Model 81 Raman spectrophotometer equipped with a Spectra-Physics Model 125 He-Ne laser for excitation. The instrument was calibrated with the emission lines from a neon lamp over the spectral range 0-4000  $\text{cm}^{-1}$ , and the frequencies for all sharp lines are expected to be accurate to  $\pm 2 \text{ cm}^{-1}$ .

For the low temperature solid study, samples were deposited at  $-170^\circ\text{C}$  onto the face of a movable brass piston mounted in a cold cell similar to the one described by Carlson<sup>11</sup> (see Fig. 4). The Raman spectra of the liquid phases were obtained from samples sealed in capillary tubes and maintained at room temperature (see Fig. 5). Polarization data were obtained from the liquid samples on a Spex Ramanlog utilizing ninety degree scattering.

## RESULTS AND DISCUSSION

It is likely that azomethane has  $C_{2h}$  symmetry since previous studies<sup>5,7,8</sup> have indicated that the methyl groups are trans to one another. Thus, the molecule is expected to have an inversion center and the principle of mutual exclusion should be operative. A comparison of the infrared and Raman frequencies (see Tables I and II) reveals no coincident frequencies for the skeletal modes and it is concluded that the molecule does indeed have a center of inversion and belongs to the  $C_{2h}$  point group. Under  $C_{2h}$  symmetry the fundamental vibrations of  $CH_3NNCH_3$  belong to the following irreducible representations:  $8a_g + 5a_u + 4b_g + 7b_u$ . The gerade (g) and ungerade (u) subscripts specify which of the normal modes are Raman or infrared active, respectively. Theoretically, the hydrogen motions should give rise to 18 of the fundamentals modes ( $5a_g + 4a_u + 4b_g + 5b_u$ ) whereas the remaining 6 vibrations result from motions of the skeletal framework ( $3a_g + 2b_u + 1a_u$ ).

In order to determine the theoretical Teller-Redlich product rule ratios for vibrational assignment purposes, it is necessary to calculate the moments of inertia. A recent electron diffraction study has provided the necessary structural parameters and Table III summarizes these quantities as well as the resulting moments of inertia for both " $d_0$ " and " $d_6$ " azomethane. The axis of the largest moment of inertia,  $I_C$ , is coincident with the  $C_2$  axis, whereas the remaining two axes are perpendicular to the  $C_2$  axis and lie in the CNNC plane. The axis of least moment of inertia,  $I_A$ , passes through all three skeletal bonds, and  $I_B$  passes through only the N=N bond. Vibrations of the  $a_u$  symmetry species should give rise to C-type bands, whereas A-B hybrids are expected for the modes of  $b_u$  symmetry. The Raman effect, the lines resulting from the  $a_g$  and  $b_g$  modes should be polarized and depolarized, respectively. Therefore, the assignment has been based upon infrared band contours and Raman depolarization values, as well as isotopic shift ratios and characteristic group frequencies. The

expected gas phase contours and depolarization values for the vibrations of azomethane have been summarized in Table IV. The normal vibrations will be discussed in the following order: (1)  $\text{CH}_3$  stretching modes, (2)  $\text{CH}_3$  bending modes, (3) the skeleton modes, and (4) combinations and overtones. The  $\text{CH}_3$  torsional vibrations will be discussed separately in the final section.

#### METHYL STRETCHING VIBRATIONS

There are six  $\text{CH}_3$  stretching fundamentals to be assigned, of which three are Raman active ( $2a_g + 1b_g$ ) and three are infrared active ( $1a_u + 2b_u$ ). The symmetric mode is expected to be strong in the Raman spectrum and of lower wavenumber than the asymmetric vibrations.<sup>12</sup> Accordingly, the symmetric stretching mode,  $\nu_2(a_g)$ , is assigned to the line at  $2916 \text{ cm}^{-1}$  in the spectrum of the liquid phase of the light compound which shifts to  $2117 \text{ cm}^{-1}$  for the deuterated compound. The corresponding frequencies for the solid phase are  $2917$  and  $2120 \text{ cm}^{-1}$ , respectively. The two asymmetric modes,  $\nu_1(a_g)$  and  $\nu_{14}(b_g)$ , are expected to have about the same frequency,<sup>12</sup> and may well be degenerate since there is probably little coupling between the methyl groups. The Raman spectra exhibits lines which can be assigned to both vibrations in all spectra except that for the liquid phase of the light molecule in which case the lines cannot be resolved. The broad line at  $2977 \text{ cm}^{-1}$  in the spectrum of liquid  $\text{CH}_3\text{NNCH}_3$  is assigned to both  $\nu_1$  and  $\nu_{14}$ ; this band splits in the spectrum of the solid into two resolvable lines,  $2982$  and  $2966 \text{ cm}^{-1}$ , which can be assigned to  $\nu_{14}$  and  $\nu_1$ , respectively. For the deuterated molecule, the two vibrations give rise to resolvable lines in both liquid and solid phases. The  $b_g$  mode appears at  $2250$  and  $2262 \text{ cm}^{-1}$  in the spectra of the liquid and solid phases, respectively. Similarly, the  $a_g$  mode is assigned to the bands at  $2227$  and  $2235 \text{ cm}^{-1}$  in the spectra recorded at room and liquid nitrogen temperatures, respectively. The polarization data summarized in Table II are consistent with these assignments, since the lines assigned to the symmetric stretches are strongly polarized and the broad bands assigned to the unresolved asymmetric stretching modes have intermediate depolarization ratios.

The  $\text{CH}_3$  stretching region in the infrared is often complicated by the presence of overtones or combination bands of the methyl deformations in Fermi resonance with the stretching fundamentals. In the case of azomethane, however, the overtones are only Raman active, but combination bands involving gerade and ungerade modes are infrared active. The  $a_u$  mode is expected to give rise to a C-type band and the  $b_u$  fundamentals should give rise to A - B hybrids (see Table IV). Since one would expect the infrared and Raman frequencies for these  $\text{CH}_3$  motions to correspond, we have assigned the two asymmetric modes to the band centered about  $2982 \text{ cm}^{-1}$ . The symmetric stretching mode can then be assigned to the A-B hybrid band whose center is  $2926 \text{ cm}^{-1}$ . The corresponding bands for the polycrystalline samples and the assigned combination bands are summarized in Table I. In the "d<sub>6</sub>" molecule the strong band at  $2239 \text{ cm}^{-1}$  has been assigned to the two asymmetric vibrations, and the symmetric mode assigned to the  $2111 \text{ cm}^{-1}$  band.

#### METHYL BENDING VIBRATIONS

The six methyl deformational modes in azomethane belong to the following irreducible representations:  $2a_g + 1a_u + 1b_g + 2b_u$ . These fundamentals have well established group frequencies<sup>12</sup> and, hence, require little discussion. For example, the asymmetric C- $\text{CH}_3$  deformations are expected to be observed at  $1450 \pm 20 \text{ cm}^{-1}$ , whereas the symmetric motion generally gives rise to a band at  $1375 \pm 5 \text{ cm}^{-1}$ .

The two asymmetric modes are assigned to the bands at 1447 and 1432  $\text{cm}^{-1}$  in the Raman spectrum of solid  $\text{CH}_3\text{NNCH}_3$  and the symmetric mode is found at 1382  $\text{cm}^{-1}$ . These bands shift to 1057, 1044 and 1035  $\text{cm}^{-1}$  in the spectrum of the deuterated compound in the solid phase, respectively. Although, the spectra of the compounds in the liquid phase lacked sufficient resolution to obtain specific frequencies or depolarization ratios for each band, the centers of the broad features corresponding to the unresolved lines are 1434 and 1042  $\text{cm}^{-1}$  for the light and heavy compounds, respectively. It is noted that West and Killingsworth<sup>5</sup> had previously assigned a band at 1442  $\text{cm}^{-1}$  to the N=N stretching motion; however, such a description is not consistent with the observed isotopic shifts. Thus, it can be concluded that the band at 1447  $\text{cm}^{-1}$  results from a methyl motion rather than from a skeletal mode since it has an isotopic shift ratio of 1.37.

Although only two bands were observed in the 1450  $\text{cm}^{-1}$  region of the infrared spectrum of gaseous  $\text{CH}_3\text{NNCH}_3$ , all three deformational modes were observed in the spectrum of the solid. The fundamentals of  $b_u$  symmetry have been assigned to the A- and B-type bands centered at 1393 and 1445  $\text{cm}^{-1}$ , respectively. The counterparts of these two bands in solid  $\text{CH}_3\text{NNCH}_3$  were observed at 1386 and 1450  $\text{cm}^{-1}$ . The third  $\text{CH}_3$  deformation belongs to the  $a_u$  symmetry species and is assigned to the band at 1433  $\text{cm}^{-1}$  (see Fig. 2). It is noted that each of the deformational bands appeared to have a low frequency shoulder

as may be seen in Fig. 2 and the frequencies of the shoulders are summarized in Table I. The splitting of the deformational modes is thought to result from in-phase and out-of-phase motions in the unit cell which would suggest that there are at least four molecules per unit cell. It appears that the inversion center is maintained in the crystal since no evidence could be found for the N=N stretching or symmetric N-N-C bending modes in the low temperature infrared spectrum. A summary of the observed infrared bands and their corresponding shifts with deuteration is given in Tables I and V.

The only methyl-group vibrations remaining to be assigned in this section are the four rocking fundamentals:  $1a_g + 1a_u + 1b_g + 1b_u$ . One might expect the assignment of these fundamentals to be complicated somewhat since the two C-N stretching vibrations are expected to occur in approximately the same frequency region. In both the infrared and Raman spectra of  $\text{CH}_3\text{NNCH}_3$ , only two bands were observed between  $900\text{--}1100\text{ cm}^{-1}$  (see Figs. 2 and 4). Initially, it was thought that the B-type band centered at  $1007\text{ cm}^{-1}$  resulted from the  $b_u$  C-N stretch and that the  $916\text{ cm}^{-1}$  Raman line resulted from the corresponding  $a_g$  motion. However, the shift factors of 1.28 and 1.20, respectively indicates that these two modes involve mainly hydrogenic motions. Therefore, the respective bands in each spectrum have been assigned to the four  $\text{CH}_3$  rocking vibrations but these modes are expected to be mixed considerably with the skeletal motions. The distinction of the  $a_u$  and  $b_u$  vibrations was based upon the observed vapor-phase contours and these results are listed in Table I.

## SKELETAL VIBRATIONS

There are six fundamental modes in azomethane that result primarily from heavy atom motions and they span the following irreducible representations:  $3a_g + 1a_u + 2b_u$ . Although the  $a_g$  and  $b_u$  vibrations must involve only motions within the molecular plane, the  $a_u$  mode will involve an out-of-plane deformation. The three  $a_g$  fundamentals may be described as a N=N stretching mode, a symmetric C-N stretching mode and a symmetric CNN bending motion. Similarly, the two  $b_u$  fundamentals will involve an asymmetric C-N stretching and CNN bending motions. Until recently very little was known about the frequency of the -N=N- stretching vibration and it was not certain whether this moiety would give rise to a characteristic group frequency. A number of recent studies<sup>13-15</sup>, however, have established that the group frequency for the N=N linkage appears to be 1530-1585  $\text{cm}^{-1}$ . In azomethane the weak Raman line centered at 1574  $\text{cm}^{-1}$  in the spectra of the solid phase has been assigned to  $\nu_3$ . Upon complete deuteration  $\nu_3$  shifts to 1561  $\text{cm}^{-1}$  which confirms the assignment to a skeletal vibration. The depolarization ratio is 0.6 for this band which indicates that it is a symmetric mode. As noted earlier West and Killingsworth<sup>5</sup> proposed a much lower frequency, but their assignment was made without the benefit of isotopic substitution. Furthermore, in a somewhat later study, Kahovec and Kohlrausch<sup>6</sup> also assigned the N=N stretch to a line at 1574  $\text{cm}^{-1}$ .

The three skeletal bending fundamentals ( $1a_g + 1a_u + 1b_u$ ) can be assigned on the basis of their relatively low frequencies and observed shift ratios. The Raman line at 584  $\text{cm}^{-1}$  in  $\text{CH}_3\text{NNCH}_3$  shifts to 531  $\text{cm}^{-1}$  in  $\text{CD}_3\text{NNCD}_3$  and has been assigned to the  $a_g$  bending fundamental. The two infrared bending modes have been observed at 362 and 312  $\text{cm}^{-1}$  in  $\text{CH}_3\text{NNCH}_3$ . The analogous bands in gaseous  $\text{CH}_3\text{NNCH}_3$  were centered at 352

and  $\sim 300 \text{ cm}^{-1}$ . The higher frequency band appears to have a distinct B-type contour and has been assigned to the  $b_u$  symmetry species (see Table I). In solid  $\text{CD}_3\text{NNCD}_3$ , the  $b_u$  and  $a_u$  bending fundamentals shifted to  $316$  and  $261 \text{ cm}^{-1}$ , respectively. It is noted that the frequency shifts upon deuteration are approximately what one would predict for these vibrations of the skeletal framework.

The two C-N stretching fundamentals may be assigned to rather weak bands in both the Raman and infrared spectra. In the Raman spectra of the liquid phases of the two molecules a band appears at  $1176$  and  $1126 \text{ cm}^{-1}$  for the light and heavy compounds, respectively. Because of the isotope shift ratio, the position of this band and the depolarization ratio of  $0.6$ , it is assigned to the symmetric carbon-nitrogen stretching mode,  $\nu_6(a_g)$ . This mode is not observed in the spectra of the solid state of either compound because of the poor signal to noise ratio. The infrared active component,  $\nu_{22}(b_u)$ , of this carbon-nitrogen stretching vibration may be assigned to the weak band which shifts from  $1300$  to  $1116 \text{ cm}^{-1}$  in the spectra of solid  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$ , respectively. Although the large isotopic shift for this band indicates that there is considerable mixing of the mode with the methyl rock of the same species,  $\nu_{23}(b_u)$ .

#### COMBINATIONS AND OVERTONES

There are several additional bands in the infrared and Raman spectra which are assigned to combinations and overtones of the various fundamentals. The Raman spectra are particularly rich in these features since all overtones are Raman active. Tables I and II show the assignments of these modes. The strong bands that are in the same region of the spectra as the C-H and C-D stretching modes are rather interesting since considerable Fermi resonance

with the fundamentals must be taking place. For instance, the line at 2057 in the Raman spectra of liquid  $\text{CH}_3\text{NNCH}_3$  is assigned to the first overtone of  $\nu_4$ . This overtone must be strongly mixed with  $\nu_2$  through Fermi resonance in order that it have such high intensity. The same must also be true for the line at 2091 which can be assigned to  $\nu_3 + \nu_8$ .

#### TORSIONAL VIBRATIONS

The torsional oscillations are expected to be the vibrations of lowest energy in azomethane. The two motions transform according to the  $b_g$  and  $a_u$  symmetry species and are respectively Raman and infrared active. In cis-2-butene<sup>16</sup> the two torsional fundamentals were split by approximately  $45 \text{ cm}^{-1}$ ; however, no such splitting is anticipated for azomethane because the two  $\text{CH}_3$  groups are trans to one another. The far-infrared spectra of gaseous  $\text{CH}_3\text{NNCH}_3$  was examined at path lengths up to 8.2 m and only a single, weak Q-branch was observed below  $300 \text{ cm}^{-1}$ . Although the weak band centered near  $215 \text{ cm}^{-1}$  is in the appropriate region for a  $\text{CH}_3$  torsion, we are hesitant to draw such a conclusion at this time because it may actually be a result of a difference tone. The assignment of the torsional fundamentals is much more certain in the spectra of solid  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$ ; therefore, the barrier height calculations have been based on the low temperature analysis.

The far-infrared spectra of polycrystalline  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  may be seen in Fig. 3. The two higher frequency bands in each spectrum

have previously been attributed to skeletal bending fundamentals and have been reproduced for the purpose of relative intensity comparisons. The band centered at  $222\text{ cm}^{-1}$  in  $\text{CH}_3\text{NNCH}_3$  (Fig. 3-A) is relatively broad and appears to be split into a doublet with components at 230 and  $215\text{ cm}^{-1}$ . In the spectrum of azomethane- $\text{d}_6$ , the corresponding band is distinctly split into a doublet and the components are separated by approximately  $14\text{ cm}^{-1}$  with the center being  $166\text{ cm}^{-1}$ . There is little doubt that the bands centered at 222 and  $166\text{ cm}^{-1}$  in the " $\text{d}_0$ " and " $\text{d}_6$ " molecules, respectively, result from the  $\text{a}_u$  torsion since no other fundamental is expected at such a low frequency. Furthermore, the observed shift ratio ( $\nu_{\text{d}_0}/\nu_{\text{d}_6}$ ) is 1.34 which certainly precludes the assignment of the band to a mode of external origin.

The Raman spectra of polycrystalline  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  is reproduced in Fig. 4. For the normal molecule a single line is observed at  $223\text{ cm}^{-1}$  which corresponds very well with the observed infrared band previously discussed. Upon deuteration, a distinct doublet is observed for the  $\text{b}_g$  torsion which is centered at  $192\text{ cm}^{-1}$ . The doublet components have frequencies of 200 and  $183\text{ cm}^{-1}$ , respectively, with the lower frequency band being the more intense. It is noted that the isotopic shift ratio (223/192) for these lines is only 1.16; however, this ratio is consistent with the Teller-Redlich' product rule calculations (see Table VI). The evaluation of the theoretical  $\tau$  for the  $\text{b}_g$  symmetry species entails, in part, a product of the ratio of both the A and B principal moments of inertia which, of course, results in the observed decrease in the isotopic shift ratio for the  $\text{b}_g$  torsional fundamental. The fact that both the  $\text{a}_u$  and  $\text{b}_g$  torsions are split into doublets is additional evidence that there are at least four molecules per unit cell in azomethane.

It should be pointed out that the assignment of the torsional mode in the Raman spectrum must be considered somewhat tentative since we could not find a corresponding band in the Raman spectrum of the liquid. We have found that the low frequency torsional modes are characterized by a number of hot bands which cause considerable broadening in the spectrum of the liquid and often makes their detection quite difficult in the fluid phases. The  $223 \text{ cm}^{-1}$  Raman line could be a librational mode around the  $I_A$  axis, but the splitting in the spectra of the heavy compound casts considerable doubt on such an assignment. Because of the tentative nature of the torsional assignment in the Raman spectrum, the far infrared data were used for the barrier calculations.

In order to evaluate the magnitude of the internal rotational barrier, we have utilized both the Mathieu equation<sup>17,18</sup> and the harmonic<sup>19</sup> approximation. The spectral data indicates that there is no interaction between the two rotors; therefore, the reduced moment of inertia was calculated in the usual manner<sup>17</sup> from the assumed geometrical parameters listed in Table III. The observed  $l \leftarrow 0$  transition in azomethane can be related to the Mathieu equation eigenvalue difference in the following fashion:

$$\Delta E_{l \leftarrow 0} = 2.25 F \Delta b_{v_0}, \quad (2)$$

where  $F$  is the reduced moment of inertia constant and  $\Delta b_{v_0}$  is the eigenvalue difference. From the observed torsional transition frequency and the calculated value of  $F$ , it is possible to solve the above equation for  $\Delta b_{v_0}$ . The eigenvalue difference is then related to the potential barrier height in the following manner:

$$V_3 = 2.25 F s, \quad (3)$$

where  $s$  is a dimensionless parameter of the Mathieu differential equation. Values of  $s$  for different values of  $\Delta b_{v_0}$  have been tabulated elsewhere<sup>18</sup>. For  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$ ,  $F$  values of  $6.71$  and  $3.74 \text{ cm}^{-1}$ ,

respectively, were calculated from the structural parameters listed in Table III. Solution of the preceding expressions for azomethane and azomethane- $d_6$  result in torsional barriers of 2.69 and 2.60 kcal/mole, respectively. It is noted that the band centers observed for the  $a_u$  torsional fundamental for each molecule were utilized in the above barrier height determinations (i.e., 222 and 166  $\text{cm}^{-1}$ , respectively for the " $d_0$ " and " $d_6$ " molecules).

One can estimate the barrier height on the basis of the harmonic approximation<sup>19</sup> simply from the observed  $l=0$  frequency and the calculated value of  $F$ :

$$V_3 = v^2/9F. \quad (4)$$

In this expression  $v$  is the observed fundamental frequency and  $F$  has previously been defined. For azomethane a harmonic barrier of 2.33 kcal/mole is deduced by using an  $F$  value of 6.71  $\text{cm}^{-1}$ . It is noted that this value is somewhat lower than that determined by the Mathieu equation, but this is the usual result since the potential function has been truncated after the second order term.

It is instructive to compare the torsional barrier determined for azomethane with those previously found in similar systems. For example, the value of  $V_3$  deduced for *N*-methyl methylenimine<sup>20</sup> from a microwave investigation was 1.97 kcal/mole. Similarly the internal rotational barrier in propylene<sup>4</sup> was observed to be 1.98 kcal/mole by microwave techniques. If one allows for the usual 5-10% frequency shift upon condensation, the barrier to internal rotation in  $\text{CH}_3\text{NNCH}_3$  may still be slightly greater than those determined for the analogous molecules. However, the barrier to internal rotation in propylene in its solid state has recently been determined to be 2.7 kcal/mole.<sup>21</sup> This molecule shows an unusually large shift in the torsional frequency upon solidification, from 180 to 225  $\text{cm}^{-1}$ . It is quite possible that azomethane exhibits the same

characteristic shift, since the molecules are similar and the barriers for the solid are identical. If this is the case, the assumption that the  $H_t$  terms in the potential functions of cyclopentene and 1-pyrazoline is a very good one and the difference in the quartic coefficient must arise mainly from the  $B_s$  term in equation (1).<sup>3</sup> Therefore the smaller inversion barrier for 1-pyrazoline as compared to that of cyclopentene results mainly from the greater ring strain at the  $\alpha$  positions and not from a marked difference in a torsional barrier about the C-N bond. Even if the shift in the torsional frequency with solidification of azomethane were not nearly as large as that for propylene, the barriers about the C-N bond would not be sufficiently different from that of the methyl group attached to a carbon-carbon double bond to account for the significant difference in the potential functions for cyclopentene and 1-pyrazoline.

#### SUMMARY AND CONCLUSIONS

The infrared and Raman spectra of  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  have been examined in detail. A vibrational assignment is suggested for the 24 fundamental modes which is consistent with the molecule having  $C_{2h}$  symmetry. The spectra on the polycrystalline samples provide evidence that there are at least four molecules per unit cell since a number of the bands were observed to be split into doublets. The crystal also appears to have a center of symmetry since mutual exclusion is clearly operative. The  $b_g$  and  $a_u$  torsional fundamentals were observed at 223 and  $222\text{ cm}^{-1}$ , respectively, for the normal molecule. From the  $1\leftarrow 0$  frequencies of the  $a_u$  torsion in solid  $\text{CH}_3\text{NNCH}_3$  and  $\text{CD}_3\text{NNCD}_3$  internal rotational barriers of 2.69 and 2.60 kcal/mole were calculated, respectively.

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## REFERENCES

1. J. R. Durig, J. M. Karriker, and W. C. Harris, *J. Chem. Phys.* 52, 6096 (1970).
2. J. Laane, *J. Chem. Phys.* 50, 776 (1969).
3. J. Laane and R. C. Lord, *J. Chem. Phys.* 47, 4941 (1967).
4. D. R. Lide and D. E. Mann, *J. Chem. Phys.* 27, 868 (1957).
5. W. West and R. B. Killingsworth, *J. Chem. Phys.* 6, 1 (1938).
6. L. Kahovec and K. W. F. Kohlrausch, *Z. Physik. Chem.* B38, 96 (1937).
7. A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta. Chem. Scand.* 24, 1230 (1970).
8. H. Boersch, *Monatsch.* 65, 311 (1935).
9. IUPAC "Tables of Wavenumbers for the Calibration of Infrared Spectrometers" (Butterworth, Washington, D.C., 1961).
10. R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, 47, 2454 (1967); 52, 1161 (1970).
11. G. L. Carlson, *Spectrochim. Acta* 24A, 1519 (1968).
12. L. J. Bellamy, The Infrared Spectra of Complex Molecules (John Wiley and Sons, Inc., New York, 1962).
13. R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Amer. Chem. Soc.* 88, 3959 (1966).
14. R. J. W. LeFèvre, M. F. O'Dwyer, and R. L. Werner, *Chem. and Ind.* 378 (1953).
15. R. S. Bly, F. B. Culp, Jr. and R. K. Bly, *J. Org. Chem.* (in press).
16. J. Bragin (private communication).
17. D. R. Herschbach, *J. Chem. Phys.* 31, 91 (1959).

18. D. R. Herschbach, Tables for the Internal Rotation Problem.  
Department of Chemistry, Howard University. These tables are  
described in J. Chem. Phys. 27, 975 (1957).
19. W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski,  
Spectrochim. Acta 21A, 231 (1965).
20. K. V. L. N. Sastry and R. F. Curl, Jr., J. Chem. Phys. 41, 77  
(1964).
21. J. R. Durig and C. W. Hawley, to be published.





Table II

Raman Spectra<sup>1</sup> of Azomethane and Azomethane-d<sub>6</sub>

Azomethane				Azomethane-d <sub>6</sub>			
Raman Solid (cm <sup>-1</sup> )	Raman Liquid (cm <sup>-1</sup> )	Relative Intensity and Polarization	Raman Solid (cm <sup>-1</sup> )	Raman liquid (cm <sup>-1</sup> )	Relative Intensity and Polarization	Isotope Shift	Assignment
			2312		VW		$\nu_3 + \nu_7$
			2288		VW		?
2982		M	2262	2250	M	1.34	$\nu_{14}$
2966	2977	M, dp	2235	2227	M, .63	1.33	$\nu_1$
			2187		VW		?
				2174	W, <.1		$\nu_4 + \nu_6$
			2155		VW, <.1		$\nu_{10} + \nu_{22}$
2917	2916	S, <.1	2120	2117	M, <.1	1.34	$\nu_2$
			2091	2092	W, sh, <.1		$\nu_3 + \nu_8$
			2053	2057	W, <.1		$2\nu_4$
1574	1580	VW, <.1	1561	1563	VW, dp	1.01	$\nu_3$
1447		S	1057		M	1.37	$\nu_{15}$
1432	1434	M, .70	1044	1042	M, .70	1.37	$\nu_4$
1411		W					?
1382	1380	W, .64	1035			1.34	$\nu_5$

Table II (continued)

1026	916	1010	1176	1125	W, .45	1.05	$\nu_6$
		VW	VW, .60	804	W	1.28	$\nu_{16}$
916	916	M, .63		765	M, .35	1.20	$\nu_7$
600		sh		704	VW		?
				518	sh		
584	589	VS, <.1		531	VS, <.1	1.10	$\nu_8$
				449	VW		
223		W		200	W	1.11	
				183	W	1.22	$\nu_{17}$

Abbreviations used: S, strong; M, medium; W, weak; V, very; sh, shoulder; p, polarized; dp, depolarized.

Table III

Structural Parameters<sup>1</sup> and Calculated Moments of Inertia for Azomethane

	$r(\text{C-N}) = 1.482 \text{ \AA}$	
	$r(\text{N=N}) = 1.247 \text{ \AA}$	
	$r(\text{C-H}) = 1.105 \text{ \AA}$	
	$\angle \text{CNN} = 112.3^\circ$	
	$\text{CH}_3\text{NNCH}_3$	$\text{CD}_3\text{NNCD}_3$
	(amu- $\text{\AA}^2$ )	(amu- $\text{\AA}^2$ )
$I_A$	12.3	18.7
$I_B$	115.7	147.5
$I_C$	121.5	153.1

1. See reference 7.

Table IV  
 Symmetry Species and Predicted Spectral Activity  
 for the Normal Vibrations of Azomethane.

Infrared	Raman	Species
	$C_{2h}$	
	$8 a_g + 5 a_u + 4 b_g + 7 b_u$	
	Active Polarized	$a_g$
Active C-type band		$a_u$
	Active Depolarized	$b_g$
Active A-B hybrid		$b_u$

Table V

Summary of the Fundamental Vibrations of Azomethane  
in the Solid Phase

Vibration number	Symmetry Species and Approximate Description of the Normal Modes	CH <sub>3</sub> NNCH <sub>3</sub> (cm <sup>-1</sup> )	CD <sub>3</sub> NNCD <sub>3</sub> (cm <sup>-1</sup> )
<i>a<sub>g</sub></i>			
1	CH <sub>3</sub> Asymmetric Stretch	2966	2235
2	CH <sub>3</sub> Symmetric Stretch	2917	2117
3	N=N Stretch	1574	1561
4	CH <sub>3</sub> Asymmetric Deformation	1432	1044
5	CH <sub>3</sub> Symmetric Deformation	1382	1035
6	C-N Stretch	1176*	1125*
7	CH <sub>3</sub> Rock	916	765
8	CNN Bend	584	531
<i>a<sub>u</sub></i>			
9	CH <sub>3</sub> Asymmetric Stretch	2966	2175
10	CH <sub>3</sub> Asymmetric Deformation	1433	1043
11	CH <sub>3</sub> Rock	1112	900
12	CNN Bend	312	261
13	CH <sub>3</sub> Torsion	222	166
<i>b<sub>g</sub></i>			
14	CH <sub>3</sub> Asymmetric Stretch	2982	2262
15	CH <sub>3</sub> Asymmetric Deformation	1447	1057
16	CH <sub>3</sub> Rock	1026	804
17	CH <sub>3</sub> Torsion	223	192
<i>b<sub>u</sub></i>			
18	CH <sub>3</sub> Asymmetric Stretch	2975	2232
19	CH <sub>3</sub> Symmetric Stretch	2911	2107
20	CH <sub>3</sub> Asymmetric Deformation	1450	1046
21	CH <sub>3</sub> Symmetric Deformation	1386	1039
22	C-N Stretch	1300	1116
23	CH <sub>3</sub> Rock	1001	921
24	CNN Bend	362	316

\*Frequencies observed only in the liquid phase spectra.

Table VI  
Teller-Redlich Product Rule Ratios

<u>Symmetry Class</u>	<u>Theoretical</u>	<u>Observed</u> <sup>1</sup>
a <sub>g</sub>	5.04	4.78
a <sub>u</sub>	3.80	3.62
b <sub>g</sub>	2.88	2.78
b <sub>u</sub>	5.13	5.10

1. Frequencies from the spectra of the polycrystalline samples, with the exception of the symmetric C-N stretching which was observed only in the Raman spectra of the liquid phase.

## List of Figures

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