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of Astrophysical Interest

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University of South Carolina, Columbia, South Carolina   29208)

Principal Investigator - James R. Durig, Professor of Chemistry

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SUMMARY OF PROGRESS

Gerard P. Kuiper[1] 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°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 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[2] and methylamine.[3] 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[4], unsymmetrical dimethylhydrazine[5], symmetrical dimethylhydrazine[6], propylene imine[7], 1-pyrazoline[8], and HNCS and

DNCS.[9] In our continued study of nitrogen containing compounds, we have completed our work on azomethane and azomethane-d_6. 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[10], trifluoromethyl peroxide[11], ethylene carbonate[12], γ-butyrolactone[12], cyclopentanone[12], oxalyl chloride[13], glyoxal[14], oxalyl bromide[15], oxalyl fluoride[16], 2,3 butanedione[17] (biacetyl), thiooxamide[18] and oxamide[18]. We have not concluded any further work in this area during this reporting period; however, studied are in progress on oxalylchlorofluoride and oxamic acid.

In a previous far infrared study[19], we analyzed the spectrum of the ring-puckering vibration of l-pyrazoline and determined that the barrier to the planar conformation was 113 cm^{-1} by using a potential function of the form:[20]

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

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 l-pyrazoline (113 cm^{-1}) was compared in a qualitative fashion with the 232 cm^{-1} barrier previously determined for cyclopentene.[21] 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 α-positions of l-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 l-pyrazoline and cyclopentene since it represents the CH_2-CH_2 torsional force. The H_t term, however, results from the torsional force about the CH_2-X bond (where X = N for l-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[22] have shown that the 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 CH_3NNCH_3 and CD_3NNCD_3 was initiated.

There have been two previous vibrational studies of azomethane[23,24] 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[23] suggest that a Raman line at 1442 cm^{-1} results from the $N\!=\!N$ stretching motion rather than a CH_3 deformational mode. Such a description does not appear to be consistent with what is now known about the $N\!=\!N$ moiety[1] since the "group frequency" appears to be 1555 ± 30 cm^{-1}. A definitive assignment of this vibration should be possible by simultaneously studying the spectrum of CD_3NNCD_3. Dipole moment and electron diffraction studies[25,26] indicate that the methyl groups in azomethane are _trans_ and the earlier vibrational data suggests mutual exclusion.

The infrared and Raman spectra of CH_3NNCH_3 and CD_3NNCD_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 cm^{-1}, respectively, for the normal molecule. From the 1←0 frequencies

of the a_u torsion in solid CH_3NNCH_3 and CD_3NNCD_3 internal rotational barriers of 2.69 and 2.60 kcal/mole were calculated, respectively. The Thermodynamic properties have been calculated for gaseous CH_3NNCH_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 thrmodynamic properties, force constants, and other useful molecularproperties 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.

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Table 1

Thermodynamic Calculations for Azomethane[*]

	S	$-(F-H_o)/T$	$(H-H_o)/T$	C_p
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	$-(F-H_o)/T$	$(H-H_o)/T$	Cp
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: $r(N{=}N) = 1.247$Å, $r(C{-}N) = 1.482$Å, $r(C{-}H) = 1.105$Å, and $\angle CNN = 112.3°$; the moments of inertia $I_A = 121.5$, $I_B = 115.7$, $I_C = 12.3$ and $I_{red} = 2.51$ (AMU)Å^2 were calculated and used in these calculations presented.

Appendix I

Vibrational Spectra and Structure of Azomethane and Azomethane-d_6

ABSTRACT: The infrared spectra of gaseous and polycrystalline CH_3NNCH_3 and CD_3NNCD_3 have been recorded from 33 to 4000 cm^{-1}. The corresponding Raman spectra of the liquid and solid samples have been measured from 100 to 4000 cm^{-1}. The vibrational data provide definitive verification of a <u>trans</u> structure with 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 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[1], we analyzed the spectrum of the ring-puckering vibration of 1-pyrazoline and determined that the barrier to the planar conformation was 113 cm^{-1} by using a potential function of the form[2]:

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

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^{-1}) was compared in a qualitative fashion with the 232 cm^{-1} barrier previously determined for cyclopentene[3]. 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 α-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_2-CH_2 torsional force. The H_t term, however, results from the torsional force about the CH_2-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[4] have shown that the 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 CH_3NNCH_3 and CD_3NNCD_3 was initiated.

There have been two previous vibrational studies of azomethane[5,6], 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[5] suggest that a Raman line at 1442 cm^{-1} results from the N=N stretching motion rather than a CH_3 deformational mode. Such a description does not appear to be consistent with what is now known about the N=N moiety[1] since the "group frequency" appears to be 1555 ± 30 cm^{-1}. A definitive assignment of this vibration should be possible by simultaneously studying the spectrum of CD_3NNCD_3. Dipole moment and electron diffraction studies[7,8] indicate that the methyl groups in azomethane are _trans_ and the earlier vibrational data suggests mutual exclusion.

EXPERIMENTAL

The samples of CH_3NNCH_3 and CD_3NNCD_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 CO_2 and the purification was followed by the relative intensity of the infrared band at 672 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[9] whereas the lower-frequency region[10] 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 cm^{-1} and the instrument was calibrated with water vapor bands[10]. 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 cm^{-1}, and the frequencies for all sharp lines are expected to be accurate to ± 2 cm^{-1}.

For the low temperature solid study, samples were deposited at -170°C onto the face of a movable brass piston mounted in a cold cell similar to the one described by Carlson[11] (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[5,7,8] 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 conicident 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) CH_3 stretching modes, (2) CH_3
bending modes, (3) the skeleton modes, and (4) combinations and overtones.
The CH_3 torsional vibrations will be discussed separately in the final section.

METHYL STRETCHING VIBRATIONS

There are six 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.[12] Accordingly, the symmetric
stretching mode, $\nu_2(a_g)$, is assigned to the line at 2916 cm^{-1} in the spectrum
of the liquid phase of the light compound which shifts to 2117 cm^{-1} for the deu-
terated compound. The corresponding frequencies for the solid phase are 2917 and
2120 cm^{-1}, respectively. The two asymmetric modes, $\nu_1(a_g)$ and $\nu_{14}(b_g)$, are
expected to have about the same frequency,[12] 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 cm^{-1} in the spectrum of liquid CH_3NNCH_3
is assigned to both ν_1 and ν_{14}; this band splits in the spectrum of the solid
into two resolvable lines, 2982 and 2966 cm^{-1}, which can be assigned to ν_{14}
and ν_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 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 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 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 fundaments. 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 CH_3 motions to correspond, we have assigned the two asymmetric modes to the band centered about 2982 cm^{-1}. The symmetric stretching mode can then be assigned to the A-B hybrid band whose center is 2926 cm^{-1}. The corresponding bands for the polycrystalline samples and the assigned combination bands are summarized in Table I. In the "d_6" molecule the strong band at 2239 cm^{-1} has been assigned to the two asymmetric vibrations, and the symmetric mode assigned to the 2111 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[12] and, hence, require little discussion. For example, the asymmetric C-CH_3 deformations are expected to be observed at 1450 ± 20 cm^{-1}, whereas the symmetric motion generally gives rise to a band at 1375 ± 5 cm^{-1}.

The two asymmetric modes are assigned to the bands at 1447 and 1432 cm^{-1} in the Raman spectrum of solid CH_3NNCH_3 and the symmetric mode is found at 1382 cm^{-1}. These bands shift to 1057, 1044 and 1035 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 cm^{-1} for the light and heavy compounds, respectively. It is noted that West and Killingsworth[5] had previously assigned a band at 1442 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 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 cm^{-1} region of the infrared spectrum of gaseous CH_3NNCH_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 cm^{-1}, respectively. The counterparts of these two bands in solid CH_3NNCH_3 were observed at 1386 and 1450 cm^{-1}. The third CH_3 deformation belongs to the a_u symmetry species and is assigned to the band at 1433 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 CH_3NNCH_3, only two bands were observed between 900-1100 cm^{-1} (see Figs. 2 and 4). Initially, it was thought that the B-type band centered at 1007 cm^{-1} resulted from the b_u C-N stretch and that the 916 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 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[13-15], however, have established that the group frequency for the N=N linkage appears to be 1530-1585 cm^{-1}. In azomethane the weak Raman line centered at 1574 cm^{-1} in the spectra of the solid phase has been assigned to ν_3. Upon complete deuteration ν_3 shifts to 1561 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[5] 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[6] also assigned the N=N stretch to a line at 1574 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 cm^{-1} in CH_3NNCH_3 shifts to 531 cm^{-1} in CD_3NNCD_3 and has been assigned to the a_g bending fundamental. The two infrared bending modes have been observed at 362 and 312 cm^{-1} in CH_3NNCH_3. The analogous bands in gaseous CH_3NNCH_3 were centered at 352

and ~ 300 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 CD$_3$NNCD$_3$, the b$_u$ and a$_u$ bending fundamentals shifted to 316 and 261 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 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 cm^{-1} in the spectra of solid CH$_3$NNCH$_3$ and CD$_3$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 CH_3NNCH_3 is assigned to the first overtone of ν_4. This overtone must be strongly mixed with ν_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[16] the two torsional fundamentals were split by approximately 45 cm^{-1}; however, no such splitting is anticipated for azomethane because the two CH_3 groups are _trans_ to one another. The far-infrared spectra of gaseous CH_3NNCH_3 was examined at path lengths up to 8.2 m and only a single, weak Q-branch was observed below 300 cm^{-1}. Although the weak band centered near 215 cm^{-1} is in the appropriate region for a 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 CH_3NNCH_3 and CD_3NNCD_3; therefore, the barrier height calculations have been based on the low temperature analysis.

The far-infrared spectra of polycrystalline CH_3NNCH_3 and CD_3NNCD_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 cm^{-1} in CH_3NNCH_3 (Fig. 3-A) is relatively
broad and appears to be split into a doublet with components at 230
and 215 cm^{-1}. In the spectrum of azomethane-d_6, the corresponding band
is distinctly split into a doublet and the components are separated by
approximately 14 cm^{-1} with the center being 166 cm^{-1}. There is little
doubt that the bands centered at 222 and 166 cm^{-1} in the "d_0" and "d_6"
molecules, respectively, result from the a_u torsion since no other
fundamental is expected at such a low frequency. Furthermore, the
observed shift ratio (ν_{d_0}/ν_{d_6}) is 1.34 which certainly precludes the
assignment of the band to a mode of external origin.

The Raman spectra of polycrystalline CH_3NNCH_3 and CD_3NNCD_3 is
reproduced in Fig. 4. For the normal molecule a single line is observed
at 223 cm^{-1} which corresponds very well with the observed infrared band
previously discussed. Upon deuteration, a distinct doublet is observed
for the b_g torsion which is centered at 192 cm^{-1}. The doublet compo-
nents have frequencies of 200 and 183 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 calcu-
lations (see Table VI). The evaluation of the theoretical τ for the
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 b_g torsional
fundamental. The fact that both the a_u and 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 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[17,18] and the harmonic[19] 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[17] from the assumed geometrical parameters listed in Table III. The observed $1 \leftarrow 0$ transition in azomethane can be related to the Mathieu equation eigenvalue difference in the following fashion:

$$\Delta E_{1 \leftarrow 0} = 2.25 \ F \ \Delta b_{v\sigma}, \qquad (2)$$

where F is the reduced moment of inertia constant and $\Delta b_{v\sigma}$ 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 $\Delta b_{v\sigma}$. The eigenvalue difference is then related to the potential barrier height in the following manner:

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

where s is a dimensionless parameter of the Mathieu differential equation. Values of s for different values of $\Delta b_{v\sigma}$ have been tabulated elsewhere[18]. For CH_3NNCH_3 and CD_3NNCD_3, F values of 6.71 and 3.74 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 cm^{-1}, respectively for the "d_0" and "d_6" molecules).

One can estimate the barrier height on the basis of the harmonic approximation[19] simply from the observed $1 \leftarrow 0$ frequency and the calculated value of F:

$$V_3 = \nu^2/9F. \qquad (4)$$

In this expression ν 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 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[20] from a microwave investigation was 1.97 kcal/mole. Similarly the internal rotational barrier in propylene[4] 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 CH_3NNCH_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.[21] This molecule shows an unusually large shift in the torsional frequency upon solidification, from 180 to 225 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).[3] Therefore the smaller inversion barrier for 1-pyrazoline as compared to that of cyclopentene results mainly from the greater ring strain at the α 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 CH_3NNCH_3 and CD_3NNCD_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 cm^{-1}, respectively, for the normal molecule. From the 1←0 frequencies of the a_u torsion in solid CH_3NNCH_3 and CD_3NNCD_3 internal rotational barriers of 2.69 and 2.60 kcal/mole were calculated, respectively.

ACKNOWLEDGMENT

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Table I

Infrared Spectra[1] of Azomethane and Azomethane-d$_6$

Azomethane					Azomethane-d$_6$					
Infrared gas (cm^{-1})	Band Type	Relative Intensity	Infrared solid (cm^{-1})	Relative Intensity	Infrared gas (cm^{-1})	Band Type	Relative Intensity	Infrared solid (cm^{-1})	Relative Intensity	Assignment
2995 R 2982 Q 2972 P	A–B	VS	2975	VS	2239	?	VS	2247 (sh) 2232 2222 (sh)	W VS W	ν_{18}
2935 R			2966 (sh)	W	2178 2122 R	?	VW	2175	VW	ν_9
2926 ctr 2918 P	A–B	VS	2911	VS	2111 ctr 2108 P	A–B		2107	W	ν_{19}
2866 R 2856 ctr 2851 P	A–B	M	2847	M	2075 R 2068 ctr 2062 P	A–B		2058 2046 (sh)	W W	$\nu_4 + \nu_{20}$
2754 R 2746 ctr 2740 P	B	W	2744	W						$\nu_{21} + \nu_5 = 2768$
1455 R 1445 ctr 1438	B	S	1450 1443		1055 (sh) 1047 Q	?	M	1046	S	ν_{20}
			1433 1421					1043 (sh)	S	ν_{10}
1393 Q	A	M	1386 1373	M	1029 (sh)	?		1039 (sh)	M	ν_{21}
1300 Q	?	VW	1330	VW				1116	VW	ν_{22}
1116 R 1109 Q 1106 Q	C	W	1112	W	894 (bd)	?	S	900	M	ν_{11}

Table I (Continued)

1015 R	B									
1007 ctr	B	W	1001	S	894 (bd)	?	S	921	S	ν_{23}
1000 P										
360 R					311 R					
352 ctr	B	M	362	S	304 Q	B	M	316	S	ν_{24}
					298 P					
305 Q (sh)										
295 Q (sh)										
285 Q	C?	M	312	S	273 Q	C	M	261	S	ν_{12}
268 Q										
230			230					173		
215		VW	215	VW				159	VW	ν_{13}

1. Abbreviations used: S, M, W, V, bd, sh, denote strong, medium, weak, very, broad, and shoulder, respectively.

Table II

Raman Spectra[1] of Azomethane and Azomethane-d_6

Azomethane			Azomethane-d_6			Isotope Shift	Assignment
Raman Solid (cm^{-1})	Raman Liquid (cm^{-1})	Relative Intensity and Polarization	Raman Solid (cm^{-1})	Raman Liquid (cm^{-1})	Relative Intensity and Polarization		
2982		M	2312		VW		$\nu_3 + \nu_7$
2966	2977	M, dp	2288	2250	VW		?
			2262		M	1.34	ν_{14}
			2235	2227	M, .63	1.33	ν_1
			2187	2174	VW		?
			2155		W, <.1		$\nu_4 + \nu_6$
2917	2916	S, <.1	2120	2117	VW, <.1		$\nu_{10} + \nu_{22}$
			2091	2092	M, <.1	1.34	ν_2
2852		M, <.1	2053	2057	W, sh, <.1		$\nu_3 + \nu_8$
2738		M, <.1			W, <.1		$2\nu_4$
							$2\nu_5$
1574	1580	VW, <.1	1561	1563	VW, dp	1.01	ν_3
1447		S	1057		M	1.37	ν_{15}
1432	1434	M, .70	1044	1042	M, .70	1.37	ν_4
1411		W					?
1382	1380	W, .64	1035			1.34	ν_5

Table II (continued)

ν	Intensity	ν	ν	Intensity	ρ	Assignment
1176	VW, .60		1125	W, .45	1.05	ν_6
1010	VW	804	792	W	1.28	ν_{16}
916	M, .63	765	764	M, .35	1.20	ν_7
			704	VW		?
600	sh	518		sh		
584	VS, <.1	531	524	VS, <.1	1.10	ν_8
			449	VW		
		200		W	1.11	
223	W	183		W	1.22	ν_{17}

(additional entries: 1026, 916)

Table III

Structural Parameters[1] and Calculated Moments of Inertia for Azomethane

$$r(C-N) = 1.482 \text{ Å}$$

$$r(N=N) = 1.247 \text{ Å}$$

$$r(C-H) = 1.105 \text{ Å}$$

$$\angle CNN = 112.3°$$

	CH_3NNCH_3 (amu-Å^2)	CD_3NNCD_3 (amu-Å^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.

$$C_{2h}$$
$$8 a_g + 5 a_u + 4 b_g + 7 b_u$$

Infrared	Raman	Species
	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_3NNCH_3 (cm^{-1})	CD_3NNCD_3 (cm^{-1})
	a_g		
1	CH_3 Asymmetric Stretch	2966	2235
2	CH_3 Symmetric Stretch	2917	2117
3	N=N Stretch	1574	1561
4	CH_3 Asymmetric Deformation	1432	1044
5	CH_3 Symmetric Deformation	1382	1035
6	C-N Stretch	1176*	1125*
7	CH_3 Rock	916	765
8	CNN Bend	584	531
	a_u		
9	CH_3 Asymmetric Stretch	2966	2175
10	CH_3 Asymmetric Deformation	1433	1043
11	CH_3 Rock	1112	900
12	CNN Bend	312	261
13	CH_3 Torsion	222	166
	b_g		
14	CH_3 Asymmetric Stretch	2982	2262
15	CH_3 Asymmetric Deformation	1447	1057
16	CH_3 Rock	1026	804
17	CH_3 Torsion	223	192
	b_u		
18	CH_3 Asymmetric Stretch	2975	2232
19	CH_3 Symmetric Stretch	2911	2107
20	CH_3 Asymmetric Deformation	1450	1046
21	CH_3 Symmetric Deformation	1386	1039
22	C-N Stretch	1300	1116
23	CH_3 Rock	1001	921
24	CNN Bend	362	316

*Frequencies observed only in the liquid phase spectra.

Table VI

Teller-Redlich Product Rule Ratios

Symmetry Class	Theoretical	Observed[1]
a_g	5.04	4.78
a_u	3.80	3.62
b_g	2.88	2.78
b_u	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 .

A

TRANSMITTANCE

WAVENUMBER (CM⁻¹)

4000   3500   3000   1600   1400   1200   1000   800   600   400   200

B

TRANSMITTANCE

WAVENUMBER (CM⁻¹)

2500   2000   1800   1600   1400   1200   1000   800   600   400   200

TRANSMITTANCE

500   400   300   200

WAVENUMBER CM⁻¹

A

TRANSMITTANCE

300   200

B

WAVENUMBER CM⁻¹

WAVENUMBER CM·¹

WAVENUMBER CM·¹

WAVENUMBER CM⁻¹