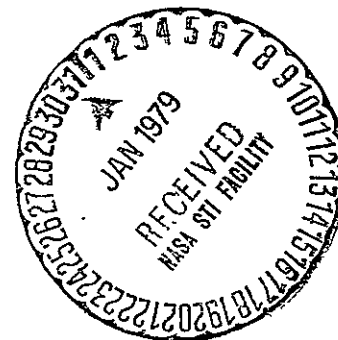


Infrared Spectra of Molecules and Materials
of Astrophysical Interest

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SUMMARY OF PROGRESS

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 planet or exist in outer space. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the composition 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, and (4) 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 photochemically¹. 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 methylamine,³ as well as several substituted hydrazines⁴⁻⁸. Recently, both ethane and acetylene have been found in the atmosphere of Jupiter⁹. It is expected that substituted ethanes will also be eventually found in some of the planetary atmospheres. In fact, ethanol has been found in the Sagittarius B12 cloud of dust and gas which is near the center of the Milky Way¹⁰. In addition, molecules such as acetaldehyde (CH_3CHO), methanol (CH_3OH), dimethylether ($\text{CH}_3)_2$), formic acid (HCOOH), have been identified in outer space.

We have continued our studies of these types of molecules with an investigation of the infrared and Raman spectra of isopropylamine. As pointed out earlier, methane and ammonia are all possible planetary atmospheric constituents and isopropylamine could possibly be produced photochemically with strong ultraviolet radiation. Thus, this molecule should be of astrophysical interest.

Isopropylamine (2-aminopropane) has been the subject of several studies in which an attempt was made to define the conformation of this molecule. Internal rotation about the C-N bond gives rise to three possible staggered conformations, where the lone pair of electrons on the nitrogen is either trans to the α C-H bond (denoted s-trans throughout) or s-trans to one of the C-C bonds, which results in two equivalent gauche conformations.

On the basis of symmetry arguments Scott and Crowder¹¹ concluded that the predominant conformation must be the gauche conformer of C_1 symmetry if their observation for two methyl torsions was correct. Later, in a statistical-thermodynamical treatment using the previous spectroscopic data to calculate the calorimetric entropy values, Scott¹² concluded that the C_s and C_1 conformations differ little in relative energy. In fact, he obtained satisfactory agreement between calorimetric and statistical values by use of a simple, three-fold, cosine type barrier for the NH_2 torsion of height $2.1 \text{ kcal/mole}^{-1}$, which was evaluated from the observed torsional fundamental of 234 cm^{-1} . This indicated that the enthalpy difference between the two conformers in the gaseous phase was close to zero. Despite the apparent evidence for the presence of two conformers he selected the C_1 conformation as the basis for his statistical calculations. The presence of two CD stretching bands for $(CH_3)_2CDNH_2$ in dilute CCl_4 solution was interpreted by Krueger and Jan¹³ as a strong indication of two conformations differing in enthalpy by $120 \text{ cal/mole}^{-1}$. Evidence was presented in this work¹³ that the low energy conformer was probably s-trans.

In a recent microwave study of isopropylamine Mehrotra et al.¹⁴ assigned the rotational spectrum arising from one conformer only. This conformer was shown to have a plane of symmetry, and it was concluded to be the s-trans, but a complete structural determination was not possible.

From molecular orbital calculations Lathan et al.¹⁵ found the conformation with the lowest energy to be s-trans with the nitrogen lone pair gauche to both methyl groups. However, they calculated the enthalpy difference between conformers in the gaseous phase to have a value of 670 cal/mole⁻¹ and suggested that the energy difference is substantially higher than the value obtained experimentally¹³ in carbon tetrachloride solution.

The presence of two methyl groups in this molecule gives rise to two methyl torsional modes which should be coupled motions because in the study on isopropyl phosphine¹⁶ a significant top-top interaction was found.

Recently, a more rigorous approach has been applied to a number of molecules containing two internal C_{3v} rotors such as dimethylether¹⁷ and propane¹⁸. These studies have shown that the observed torsional transitions can only be satisfactorily explained by using a two dimensional treatment of the torsional potential function. Substitution of a hydrogen, in propane, by an amino group may result in a complication of the torsional spectrum by not only the addition of the amino torsion but also by changing the methyl torsional potential function along with the possible presence of two conformers.

As pointed out earlier, Krueger and Jan¹³ as well as Lathan et al.¹⁵ have concluded that the s-trans conformer is the most stable one. If this is true, then the previous vibrational assignments^{11,12} and statistical-thermodynamics¹² need further examination; therefore, we have recorded the Raman and infrared spectra of all three phases, with special attention paid to the important Raman depolarization and torsional data. We hoped to resolve the existing literature discrepancies concerning the conformation analysis, vibrational assignments, torsional potential functions, and the gaseous phase thermodynamic functions.

The results of this study have been submitted for publication in the Journal of Physical Chemistry. The complete paper is given as Appendix I at the end of this report and we shall summarize our results below with the abstract from the paper.

ABSTRACT: The Raman spectra of gaseous, liquid and solid, and infrared spectra of gaseous and solid isopropylamine-d₀ and -d₂ have been investigated between 4000 and 50 cm⁻¹. Differences between the spectrum of the solid phase and that of the fluid phases have been interpreted in terms of an equilibrium between low energy s-trans and high energy gauche conformers, and a complete vibrational assignment has been proposed for the s-trans conformer. The far infrared spectra of the gaseous compounds contained bands due to the asymmetric amino and coupled methyl torsions; the assignment of these bands was aided by observation of a number of two quantum transitions for each vibrational mode. The asymmetric potential functions were calculated, which resulted in values for the enthalpy differences between conformers in the gaseous phase of 446 and 523 cal/mole for the -d₀ and -d₂ compounds, respectively. The methyl torsional potential function of isopropylamine-d₀ was calculated which led to a value for the barrier height to internal rotation of the methyl rotors of 4.23 ± 0.06 kcal/mole. Values for the ideal gas thermodynamic functions have been calculated over a range of temperatures.

FUTURE WORK

We have undertaken a vibrations study of the low frequency spectrum of isopropyl alcohol. The spectral data are extremely complicated and there appears to be significant coupling of the hydroxol torsion with the two methyl torsions. Similar work has been initiated on isopropyl sulfide. Work has been initiated on disilylamine with the preparation completed. Vibrational studies have been undertaken but the progress is rather slow. We have also initiated a microwave study of $\text{CH}_3\text{SiH}_2\text{PH}_2$ and we hope to finish this work by the next reporting period. We also hope to begin the vibrational studies on azoethane. We shall also continue our current work on several compounds which have potential interest as planetary atmosphere materials.

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APPENDIX

Analysis of Torsional Spectra of Molecules with Two Internal C_{3v} Rotors.
XIV.* Vibrational Assignments, Torsional Potentail Functions and Gas Phase
Thermodynamic Functions of Isopropylamine- d_0 and $-d_2$.

ABSTRACT

The Raman spectra of gaseous, liquid and solid, and infrared spectra of gaseous and solid isopropylamine- d_0 and $-d_2$ have been investigated between 4000 and 50 cm^{-1} . Differences between the spectrum of the solid phase and that of the fluid phases have been interpreted in terms of an equilibrium between low energy s-trans and high energy gauche conformers, and a complete vibrational assignment has been proposed for the s-trans conformer. The far infrared spectra of the gaseous compounds contained bands due to the asymmetric amino and coupled methyl torsions; the assignment of these bands was aided by observation of a number of two quantum transitions for each vibrational mode. The asymmetric potential functions were calculated, which resulted in values for the enthalpy differences between conformers in the gaseous phase of 446 and 523 cal/mole for the $-d_0$ and $-d_2$ compounds, respectively. The methyl torsional potential function of isopropylamine- d_0 was calculated, which led to a value for the barrier height to internal rotation of the methyl rotors of 4.23 ± 0.106 kcal/mole. Values for the ideal gas thermodynamic functions have been calculated over a range of temperatures.

INTRODUCTION

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The isopropylamine sample was purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis. Its deuterated amino analog was prepared by allowing isopropylamine to exchange in 20:1 excess D_2O , separating the amine, and repeating the process three times. The progress of the deuteration was followed by observing the decrease in intensity of the NH stretch. The final isotopic purity was estimated to be approximately 98%. Sample purifications were performed by using fractional condensation (trap-to-trap) methods or, more generally, a low temperature, low pressure fractionating column.

Infrared spectra between $4000-200\text{ cm}^{-1}$ were recorded on a Perkin-Elmer Model 621 spectrophotometer with an extended base and was purged with dry nitrogen and calibrated with frequencies of atmospheric water vapor⁹ and standard gases¹⁰. Spectra of the gaseous phase were obtained by using a 10-cm cell with CsI windows and typically 7 torr of sample pressure. For studies of the solid phase, a vacuum cold cell similar to that described previously¹¹ with outer windows and sample substrate fashioned from CsI was used.

Far infrared spectra ($520-40\text{ cm}^{-1}$) were obtained by using a Digilab FTS-15B Fourier transform interferometric spectrometer. A 6.25 micron beam-splitter and high pressure Hg arc lamp source were used. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. Spectra of the gaseous phases were obtained by using a 12-cm cell with polyethylene windows and about 30 torr of sample pressure. Interferograms for both the sample and empty reference cell were recorded 2500 times, averaged, and transformed using a boxcar apodization function. Spectra of the solid phase samples were obtained by condensing the compound onto a Si plate maintained at $\sim 15^\circ\text{K}$ by a closed-cycle helium refrigerator. All far infrared spectra of the gaseous phase were recorded at an effective resolution of better than 0.5 cm^{-1} , whereas the spectra of the solid phase were recorded at 2 cm^{-1} resolution.

All Raman spectra were recorded to 4000 cm^{-1} with a Cary Model 82 spectrophotometer equipped with a Coherent Radiation Model 53A or a Spectra Physics

171 argon ion laser operating on the 5145 Å line. For studies in the liquid and solid phase, the laser power at the sample was typically 0.5W, whereas for the gas phase studies, maximum power of nearly 3W at the sample was used. The instrument was calibrated with mercury and neon emission lines. Gaseous samples were held at their room temperature vapor pressure (420 torr) in quartz cells similar to standard Cary multipass cells. Spectra of the liquids were recorded from samples sealed in glass capillaries. A sealed capillary was also used for studies of low temperature liquid and solid samples in a Harney-Miller cell¹². Frequency measurements for sharp, resolvable bands are expected to be accurate to at least $\pm 2 \text{ cm}^{-1}$.

RESULTS

The Raman spectra of gaseous, liquid, and solid isopropylamine- d_0 and -d_2 are shown in Figs. 1 and 2 respectively; the mid-infrared spectra for gaseous and solid phases of these compounds are shown in Figs. 3 and 4, respectively.

The observed frequencies and assignments for isopropylamine- d_0 and -d_2 are given in Tables I and II, respectively. The vibrations are numbered relative to the s-trans conformer of isopropylamine- d_0 and the approximate descriptions of the fundamental modes are given in Table III.

The far infrared spectra of gaseous isopropylamine- d_0 and isopropylamine- d_2 at 0.5 cm^{-1} resolution between 500 and 80 cm^{-1} are shown in Fig. 5. The observed far infrared and Raman torsional transitions of the two gaseous compounds below 520 cm^{-1} with proposed assignments are listed in Tables IV and V.

Vibrational Assignment

The s-trans conformer has a plane of symmetry and belongs to the C_s point group, and the vibrations span the irreducible representations: $18\text{A}'$ and $15\text{A}''$. In the Raman spectra of the fluid phases the A' modes give rise to polarized lines while A'' modes should be depolarized. From calculations, one predicts that

the infrared band contours of the gas phase will be A/B for A' modes and C for A'' modes. The two equivalent gauche conformers have only the identity element of symmetry and belong to the point group C_1 . With this symmetry, the vibrations of the gauche conformers are all A modes and should be polarized in the Raman spectra of the fluid phases, and have hybrid A/B/C band contours in the infrared spectrum of the gas.

The Raman spectra of the gaseous and liquid phases show a number of depolarized bands which generally correspond to C type infrared band contours in the gaseous phases. These data are evidence of the presence of the s-trans conformer. On freezing the liquid samples, a number of polarized bands were noted to disappear from the Raman spectra; in general, the depolarized bands in the liquid did not disappear which indicates that the s-trans conformer is more stable than the high energy gauche conformer. On this basis, bands present in the spectrum of the solid were assigned as s-trans bands, whereas new bands observed in the fluid phases were assumed to be due to the gauche conformer.

Assignments of the fundamental vibrations were based on the existing assignments of similar molecules along with the information provided from isotopic shift on deuteration of the amino group. In general, the assignments of the vibrations involving the amino group follow those given for methylamine¹³, and the remaining vibrations follow the assignments given for isopropylphosphine⁶. The final assignment, presented in Table III, was checked using the Teller-Redlich product rule. The theoretical product ratios (d_2/d_0) for the A' and A'' blocks were calculated to be 0.355 and 0.346, and the experimental frequencies listed in Table III gave ratios of 0.367 and 0.355, respectively.

The N-H and N-D stretches are of prime importance since they are well separated in frequency from the other fundamental modes and these modes are also sensitive to the amino conformation. The strongest band at 3342 cm^{-1} in this region of the Raman spectrum was polarized and it was assigned to the symmetric stretch of the

s-trans conformer while the weak depolarized band at 3411 cm^{-1} was assigned to the corresponding antisymmetric stretch. The weaker bands at 3393 and 3328 cm^{-1} in the gaseous phase were assigned to the NH_2 stretches of the gauche conformer. Close examination of the Raman spectrum of gaseous isopropylamine- d_2 showed a number of bands near 2400 cm^{-1} . The strongly polarized band at 2447 cm^{-1} was assigned to the ND_2 symmetric stretch of the s-trans conformer while the weak depolarized band at 2532 cm^{-1} was assigned to the antisymmetric stretch of the same conformer. The assignment of the N-D stretches of the gauche conformer was ambiguous. One band at 2402 cm^{-1} in the gaseous phase corresponded to one band at 2390 cm^{-1} in the liquid which disappeared in the solid. There were two other bands at 2492 and 2458 cm^{-1} in the gas phase and the former one was close to the frequency of the s-trans antisymmetric stretch and was considered to be the other ND stretch of the gauche conformer. Similar effects were observed for isopropylphosphine⁶ and cyclobutylamine¹⁴, where four bands in the spectrum of the gas phase are reduced to three bands in the spectrum of the liquid.

The amino group has three bending modes, the scissor, twist and wagging vibrations, which have previously¹⁵ been assigned to bands at 1622 , 1252 and 782 cm^{-1} , respectively. The scissor and wag assignments have not been altered; however the assignment of the twisting mode has been revised to 1352 cm^{-1} . A vibrational assignment of methylamine and three deuterated species¹³ showed that the $-\text{NH}_2$ twist was very weak in both the Raman and infrared spectra and hence very hard to locate. The twist in CH_3NH_2 was assigned¹³ to a band at 1353 cm^{-1} and in CH_3ND_2 , at 1130 cm^{-1} , both solid phase frequencies, and the corresponding selected values in isopropylamine were 1352 and 1014 cm^{-1} in the solid phases.

The C-N stretching mode was assigned to bands observed to be relatively strong in the Raman spectrum and weak in the infrared. This mode was found to be sensitive to the orientation of the $-\text{NH}_2$ group. In the "light" compound, the spectra of the gaseous phase is complicated while the corresponding spectra of the $-\text{d}_2$

compound is simpler. In the Raman spectrum of the deuterated molecule in the gaseous phase, a strong band at 803 cm^{-1} has been assigned as the C-N stretch of the s-trans conformer. An additional feature at 788 cm^{-1} in the gaseous phase and absent in the solid phase has been assigned as the C-N stretch of the high energy gauche conformer. A similar conclusion can be drawn from the Raman spectrum of the light compound.

The low frequency bending modes of the heavy atom skeleton were assigned by comparison with the corresponding modes of isopropylphosphine⁶. The C-C-C bends in the phosphine-d₀ and -d₂ molecules were assigned to frequencies of 388 and 380 cm^{-1} respectively. The corresponding bends in the amines were expected to have frequencies only slightly higher than the phosphine because of the small contribution to this mode from the phosphorous or nitrogen atoms. The bands observed at 404 and 381 cm^{-1} were assigned to this mode in the -d₀ and -d₂ molecules, respectively; the rather large isotopic shift observed indicates a different potential energy distribution in the vibrational mode of each isotope. The C-C-N in-plane and out-of-plane bending modes were observed close together in the spectrum of isopropyl phosphine, at 325 and 322 cm^{-1} , respectively, with the latter mode being weaker and difficult to observe. The lower mass of the amino group should result in these modes shifting up in frequency to approximately 390 cm^{-1} but assuming that the above C-C-C bend assignment is correct, the shift is larger than expected. The only other suitable assignment for the in-plane bend is to the polarized Raman band at 472 cm^{-1} . The out-of-plane mode was assigned to the very weak band at 369 cm^{-1} , corresponding to the medium polarized band at 374 cm^{-1} in the Raman spectrum of the liquid.

The modes associated with the isopropyl moiety of the molecule, in general, have similar frequencies to the corresponding modes of isopropylphosphine⁶. Assignments of CH stretching fundamentals are ambiguous because of the poor band contour and depolarization data, and also because of the possibility of overtone and combination bands which are often found in this region. In particular,

identification of A'' modes was hampered by the lack of depolarized Raman bands. Several of the isopropyl modes were very weak and difficult to identify. In particular, the CH in-plane and out-of-plane deformations were not easy to assign, but because these modes were observed to be close together in isopropylphosphine, both have been assigned to weak bands near 1245 cm^{-1} in the spectra of the light compound. Similarly, the methyl rocking modes were hard to locate because of the complex nature of the spectra near 950 cm^{-1} , and the proposed assignments in this region must be considered tentative.

Torsional Assignments and Barriers to Internal Rotation

The isopropylamine molecule exhibits two types of torsional motion: the amino torsional motion due to internal rotation about the N-C bond and the two methyl torsional modes. The far infrared and the Raman spectra of the gaseous phases of $-d_0$ and $-d_2$ were examined very carefully and were compared with other similar molecules with the hope of observing bands assignable to the torsional modes of the methyl and amino groups.

The low frequency vibrational data of the gaseous $-d_0$ and $-d_2$ compounds are listed in Tables IV and V and the far infrared spectra are shown in Fig. 5. The far infrared spectra of both molecules are complex, especially in the regions near 500 cm^{-1} and below 300 cm^{-1} . In the spectrum of the $-d_0$ compound, a number of very strong bands were observed between 270 and 180 cm^{-1} . Initial comparison with the spectrum of the $-d_2$ compound indicated that all of these bands were due to the $-\text{NH}_2$ group because a similar pattern of bands was observed in the spectrum of the $-d_2$ compound below 195 cm^{-1} . However, close analysis showed that the strongest band in the $-d_0$ spectrum at 236 cm^{-1} does not, in fact, shift in frequency. All of the other strong bands below 270 cm^{-1} shift down in frequency by a factor of nearly 0.7. This indicates that the 236 cm^{-1} band, and satellites at 233 and 231 cm^{-1} , are due to methyl torsions, whereas all due to amino torsions. In the spectrum of the heavy compound, very weak bands were observed near 236 cm^{-1} , and these are, therefore, assigned as methyl torsions

for this compound. The large difference in intensity of the methyl torsions observed for the $-d_0$ and $-d_2$ compounds initially appears puzzling, but a similar effect has been noted previously in the spectrum of ethylamine¹⁶. The spectrum of ethylamine- d_0 showed moderately strong bands near 250 cm^{-1} which were assigned to methyl torsions, but these bands were very weak in the deuterated compound¹⁷. It was concluded¹⁵ that coupling between the methyl and amino torsions enhanced the intensity of the methyl torsion, but on deuteration this coupling was removed by lowering the amino torsional frequency.

Amino Torsion

The far infrared spectra of both compounds showed two series of bands which could be attributed to amino torsional vibrations. Normal potential functions generally result in the torsions of a high energy conformer having lower frequencies than those of the stable conformer. On this basis, the s-trans and gauche amino torsional fundamentals were assigned to the bands at 267 and 220 cm^{-1} for $-d_0$ compound and 195 and 171 cm^{-1} for the $-d_2$ compound respectively, even though the high frequency torsional series was observed to be weaker in intensity in both compounds.

The potential functions for the amino torsions were calculated using the torsional assignments listed in Tables IV and V. The reduced rotational constant was calculated as a function of the angle of internal rotation, α ,

$$(F_{\alpha} = F_0 + \sum_i F_i \cos i\alpha)$$

defined as zero for the s-trans conformer, using the structure proposed for the light compound by microwave spectroscopy⁴. The observed frequencies were fitted to a potential function by varying the torsional angle, α ,

$$V_{\alpha} = 1/2 \sum_i V_i (1 - \cos i\alpha).$$

For initial calculations, the enthalpy difference between the lowest gauche and s-trans energy level, ΔH , was assumed to be 40 cm^{-1} as calculated for the liquid phase². However, in order to fit the observed frequencies adequately a much larger

value of ΔH was required. The program allowed variation of ΔH , (entered as a forbidden transition) so ΔH was given a low weighting and allowed to vary. The final potential function calculated for the $-d_0$ compound is shown in Fig. 6. The calculated potential coefficients, with dispersions and values of ΔH , are given in Table VI.

Assignment of the $-d_2$ amino torsions was aided by identification of a number of two quantum transitions in the far infrared spectrum; in particular the higher s-trans single jump frequencies, which were observed to be weaker than the gauche bands, were identified only by the two quantum transitions. The identified single jump s-trans transitions gave evidence of an unusual potential function; the first two transitions were observed close together near 190 cm^{-1} , but the next transition was observed at 171 cm^{-1} . This may be because of the close proximity of the two quantum transition to the ν_{12} bend at 380 cm^{-1} which results in the possibility of Fermi resonance interaction between the torsional energy level and that of the bend. Close examination of Table V shows that the proposed potential function predicts the gauche torsional frequencies well but cannot predict the s-trans frequencies as accurately.

The s-trans conformer of isopropylamine has two methyl torsions, one symmetric (A') and the other asymmetric (A'') to the plane of symmetry, but because the methyl tops are in equivalent environments, the barrier heights are equal and the system can be labelled⁷ $C_s(e)$ where e represents equivalent tops. However, the gauche conformer, being of C_1 symmetry, has two separate methyl top environments because one top is gauche to the nitrogen lone pair, and so is labelled as a $C_1(n)$ system where n represents non-equivalent tops. The gauche methyl torsions are both necessarily A modes and have different barrier heights.

Close examination of the far infrared spectrum of the $-d_2$ compound in the gaseous phase showed a number of very weak bands above 230 cm^{-1} , the strongest of these bands being at 236.2 and 232.6 cm^{-1} . In the light compound, a series of bands were observed at 236.0 cm^{-1} and lower frequency and so these bands were

assigned as methyl torsions. These bands did not coincide with any polarized Raman bands which would allow their assignment to gauche modes and so they have been assigned to the s-trans conformer, which was expected to show stronger bands due to its higher concentration.

The strong band at 236 cm^{-1} in the far infrared spectrum of isopropylamine- d_0 has already been assigned as a methyl torsion in the previous section, and the bands at 232.6 cm^{-1} (medium) and 230.2 cm^{-1} (very weak) appear to be higher transitions in a series because of their relative intensities. This conclusion was confirmed by observation of the weak two quantum transitions at 468.8 ($236.1 + 233.0 = 469.1$) and 464.3 ($233.0 + 230.7 = 463.7$) cm^{-1} . This series of bands was assigned to the lower frequency methyl torsion of the s-trans conformer which should show C type bands and belong to the A'' representation, although there is a possibility that these bands are the corresponding gauche transitions. The higher frequency series of bands due to the A' torsional mode was observed as a number of very weak bands close to the s-trans amino torsions in the region between 260 and 240 cm^{-1} because more bands were observed here than could be accounted for by the amino torsion alone, and two quantum transitions were observed near 500 cm^{-1} . The large difference in intensity between the two series is taken as evidence that these vibrations belong to the A' and A'' representations of the s-trans conformer; the gauche modes should show more equal intensities as they are both A modes. On this assumption, the analysis of the methyl torsions of isopropylamine- d_0 was performed in the following manner.

The internal rotational Hamiltonian for the methyl torsions of the s-trans $C_s(e)$ molecule has been derived⁷ as:

$$H_I = 1/2 [g_{P_0}^{44} p_0^2 + g_{P_0 P_1}^{45} p_0 p_1 + g_{P_1}^{55} p_1^2] + 1/2 [V_{30}(1 - \cos 3\tau_0) + V_{60}(1 - \cos 6\tau_0) + V'_{60} \sin 6\tau_0 + V_{03}(1 - \cos 3\tau_1) + V_{06}(1 - \cos 6\tau_1) + V'_{06} \sin 6\tau_1 + V_{33}(\cos 3\tau_0 \cos 3\tau_1 - 1) + V'_{33} \sin 3\tau_0 \sin 3\tau_1 + V''_{33} \sin 3\tau_0 \cos 3\tau_1 + V'''_{33} \cos 3\tau_0$$

$\sin 3\tau_1]$, where $V_{30} = V_{03}$, $V_{60} = V_{06}$, $V'_{60} = -V'_{06}$, $V''_{33} = -V'''_{33}$, and $g^{44} = g^{55}$. The kinetic coefficients g^{44} etc., were calculated using the structure calculated from the microwave spectrum⁴, and are given in Table VII.

Initial calculations using the bands at 258.2, 253.1, 236.1 and 233.0 cm^{-1} as the 01 \leftarrow 00, 02 \leftarrow 01, 10 \leftarrow 00 and 20 \leftarrow 10 transitions indicated that the distance between the 01 \leftarrow 00 and 10 \leftarrow 00 transitions required a substantial value (approximately -100 cm^{-1}) for the sine-sine coupling term V'_{33} in order to fit the data. Addition of higher transitions was performed sequentially while varying $V_{30} = V_{03}$, $V_{60} = V_{06}$, V_{33} and V'_{33} , simultaneously. The parameters $V'_{60} = -V_{06}$ and $V''_{33} = -V'''_{33}$ were found to be insignificant and so were held to zero. The final fit using 12 transitions resulted in the values for the potential coefficients shown in Table VII. The effective barrier to internal rotation can be calculated from $V_{30} - V_{33}$. Because of the high correlation between these two coefficients, the dispersion on the barrier is lower than those of the individual coefficients.

A number of attempts were made to assign the observed transitions for the methyl torsions in the $-d_2$ compound, but these proved futile. The reasons for this are two fold. First, there is an inherent weakness of the one quantum transitions, and second, the two quantum transitions are near the bending mode at 450 cm^{-1} , which apparently results in some Fermi-type interaction between the bend and torsional overtones. Initial calculations indicated, however, that the barrier in the $-d_2$ compound is approximately 50 cm^{-1} higher than in the light compound.

Thermodynamic Functions

The ideal gas phase thermodynamic functions were recently calculated for isopropylamine by Scott². For these calculations, it was assumed that only the gauche conformer was present in the gaseous phase, and that all of the observed

bands could be assigned to this conformer. The vibrational assignment given in Table III is substantially different from that used previously; also the s-trans conformer has been concluded to be the low energy conformer in equilibrium with the high energy gauche form. The mixing of conformers in the gaseous phase leads to an increase in the values of the thermodynamic functions, and this increase must be taken into account when calculating the thermodynamic functions. Hence, new values of the functions have been calculated and are presented in Table VIII.

A method has been used recently by one of the authors¹⁸ to calculate the thermodynamic functions of an ideal gas existing as a mixture of conformers which uses the calculated functions for each conformer and the enthalpy difference between those conformers, ΔH . These data are used to calculate the concentration of the high energy conformer, χ_g , at each temperature, T , which then allows calculation of the final values of the thermodynamic functions. For the full discussion of the method used, the reader is referred to previous calculations on compounds existing as a mixture of conformers¹⁸.

It is important to realize the limitations of such calculations and the errors inherent in them. The normal assumptions for any statistical thermodynamical calculations have been made, i.e., rigid rotor approximation, neglect of vibration-rotation interaction, neglect of vibrational anharmonicity and the assumption that each vibrational mode is independent. In the case of the present calculations, the following factors can be considered as possible sources of error. Hydrogen bonding between molecules is present in amines although the extent of this is apparently low in isopropylamine in the gaseous phase because the hydrogen bonded N-H stretches are relatively weak. The coupling between the methyl tops has been taken account of in the barrier height, but the contribution of each of the methyl torsions to the functions has been calculated simply from the barrier height and reduced moment of inertia using published tables. The asymmetric torsions have necessarily been considered to be harmonic oscillators which clearly is an

oversimplification.

The assignment of the high energy conformer has only been partially made, hence the contribution from this conformer is not wholly accurate. The lack of information on the methyl torsions of this conformer is probably the largest source of error since the same barrier for both conformers has been assumed. The theory used in calculating the contributions due to the mixing of conformers assumes that the conformers have a long life relative to the torsional vibration. This assumption is realistic for high barriers to internal rotation for the asymmetric torsion, but may be less realistic for the lower barriers present in this molecule, because population of levels above the barrier will increase the rate of interconversion at higher temperatures. It is not possible to estimate errors on the calculated functions, but the largest errors present will probably arise from the torsional contributions which will have little effect at room temperatures but a larger effect at the higher temperatures.

CONCLUSIONS

This study has shown that in order to fully characterize the conformational properties of a molecule such as isopropylamine, it was necessary to record both infrared and Raman spectra for three phases, even though all vibrational modes are allowed in both the Raman and infrared spectra. The gas phase band contour and depolarization data from the liquid phase taken together were good evidence that a significant amount of s-trans isopropylamine is present in the fluid phases, and comparison with the spectra of the solid phase showed that a number of bands, not due to the s-trans conformer, were also present in the gas and liquid phases. Previous studies^{1,3} on this compound have not been able to report the complete spectral data, hence the conclusion that the gauche conformer was more stable must now be revised.

The low frequency region of the infrared spectrum was especially useful as it allowed complete characterization of the torsional potential functions of gaseous isopropylamine. A number of relatively strong bands have been assigned as the asymmetric torsions of both conformers in the far infrared spectra of both the $-d_0$ and $-d_2$ species, and the assignment of these bands location of a number of two quantum transitions. The potential functions calculated for the two compounds are essentially the same, although that for the $-d_0$ compound (Fig. 6) showed slightly higher barriers to internal rotation and lower ΔH , the enthalpy difference between the lowest gauche and s-trans energy levels. The resulting potential coefficients used to fit the torsional data are shown in Table VI, and it can be seen that the two sets of coefficients do differ. This difference between the two functions is assumed to arise from a different amount of coupling between the asymmetric torsion and other vibrational modes. However, two important points must be noted about these calculations: firstly, the potential functions show a significant dependence on coefficients V_4 and V_5 even though it is not possible to understand where these arise in physical terms, and secondly, the spectrum of the $-d_2$ compound showed evidence of some perturbation of the s-trans asymmetric torsional energy levels which may explain why the calculated functions differ. The s-trans $3\leftarrow 2$ and $4\leftarrow 3$ transitions were observed to be very close to the gauche $1\leftarrow 0$ and $2\leftarrow 1$ transitions, respectively, and although it is easiest to think of the s-trans and gauche torsions as separate entities, they both have part of their wavefunctions in the energy well of the other conformer, and possibly the two series of transitions are interacting by virtue of their similar frequencies.

The value of ΔH calculated for gaseous isopropylamine- d_0 , 446 kcal/mole, is significantly larger than the previous value³, 120 cal/mole, measured on $(CH_3)_2CDNH_2$ in CCl_4 solution. The gaseous compound should be more ideal because,

unless the solution is very weak, the gaseous isopropylamine molecules are much better separated. The lower ΔH in solution is therefore attributed to hydrogen bonding which should lower the gauche energy relative to the s-trans conformer. Molecular models indicate that the approach of a second molecule for hydrogen bonding is not as easy in the s-trans conformer due to the proximity of the α -hydrogen to the free hydrogens on the nitrogen atom. Hence it is reasonable to suggest that the gauche conformer will be more stabilized in the solution phase by the higher probability of hydrogen bonding. It is interesting to note that the conformational properties predicted for isopropylamine by ab initio molecular orbital calculations⁵ have been qualitatively upheld by the results of this study, since the s-trans conformer was calculated to be more stable than the gauche by 670 cal/mole⁵.

Kreuger and Jan³ discussed the relative stability of the possible conformers in isopropylamine in terms of an overlap between the nitrogen lone pair and the α C-H bond σ^* orbital. This orbital overlap is only possible in the s-trans conformer which should, hence, be stabilized relative to the gauche. An alternative explanation for the stability of the s-trans conformer can be found in terms of the "gauche effect". This effect predicts¹⁹ that the more stable conformer is the one which has the maximum number of gauche interactions between lone pairs and polar bonds on the adjacent atom. In isopropylamine the C-CH₃ bonds are more polar than the α C-H bond, and the maximum number of gauche interactions is to be found in the s-trans conformer where the lone pair is gauche to both methyl groups.

The far infrared spectrum of isopropylamine-d₀ also gave sufficient information to fully characterize the methyl torsional potential function of this molecule. The value calculated for the effective barrier height, 4.23 ± 0.06 kcal/mole, is almost the same as that calculated for isopropylphosphine-d₀, 4.49 kcal/mole⁶, but as expected it is higher than the barriers calculated for ethylamine¹⁷ and

propane⁸, 3.71 and 3.26 kcal/mole, respectively. Unfortunately, the methyl torsions of the gauche conformer could not be assigned, but it is expected that the barriers should not differ greatly from the value for the s-trans conformer. The values calculated for the cosine-cosine and sine-sine coupling terms in the isopropylamine system, 196 and 102 cm⁻¹, respectively, indicate that the methyl torsions in this molecule are strongly coupled.

The values calculated for the gaseous phase thermodynamic functions of isopropylamine-d₀, presented in Table VIII, are significantly different from the previously published values². The differences arise from the different treatment of the torsional potential functions used. Scott² used a gauche conformer as a basis for his calculations, but this only affects the entropy values slightly. More importantly, he concluded that ΔH^\ominus was approximately zero since experimental and theoretical results could be matched by use of a simple three-fold barrier for the amino torsion. The methyl torsional barriers used in the previous work² were 4.4 and 2.7 kcal/mole, and as shown above, the latter value is clearly too low. Also evidence has been put forward that the enthalpy difference between conformers is significant and the barriers to internal rotation around the C-N bond are some 50% higher than calculated by Scott². The thermodynamic functions are relatively sensitive to the torsional barriers, and so the new values for the thermodynamic functions should be more accurate than the previously published values since they are based on a more detailed analysis of the torsional potential functions. Indeed, considering the differences between the two statistical treatments used, it is surprising that the differences between the two sets of values are not much larger.

The calculated gauche concentration at normal temperatures is approximately 48%, which explains the presence of strong gauche bands in the vibrational spectrum.

ACKNOWLEDGEMENT

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Table I. Vibrational frequencies and assignments for isopropylamine-d₀^a

| INFRARED | | | | RAMAN | | | | ASSIGNMENT | | | |
|------------------|-------|------------------|-------|------------------|-----------|------------------|-----------|------------------|-------|-----------|----------------------------------|
| GAS | | SOLID | | GAS | | LIQUID | | SOLID | | Conformer | Vibration |
| cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | | |
| | | | | | | | | 3348 | m | | |
| | | | | 3411 | w, dp | 3365 | m, mp | 3218 | s | t | v ₁₉ |
| | | | | 3393 | w, sp | | | | | g | v ₁₉ |
| 3335 | w, A | 3210 | s, br | 3342 | s, sp | 3311 | m, sp | 3173 | s | t | v ₁ |
| | | | | 3328 | m | | | | | g | v ₁ |
| | | | | 2986 | m, sp | | | | | | |
| 2976 | m, A | 2970 | sh | 2979 | m, sp | | | | | | |
| | | | | 2968 | vs, sp | | | 2970 | vs | t | v ₂ |
| | | | | | | 2961 | vs, mp | | | | |
| 2965 | vs, C | 2960 | vw | | | | | | | t | v ₂₀ |
| | | 2950 | vs | 2945 | vs, sp | | | 2957 | vvs | t | v ₃ |
| 2950 | m, sh | | | | | | | 2948 | vs | t | v ₂₁ |
| 2926 | m, sh | 2925 | m, sh | 2932 | vs, sp | 2932 | vs, sh | 2918 | vs | t | v ₄ |
| | | | | 2918 | m, sp | 2920 | vs, sp | | | g | v ₄ |
| 2904 | m, sh | 2909 | m, sh | | | | | | | | |
| | | | | 2888 | s, sh, sp | | | | | | |
| 2876 | m | 2870 | s, sh | 2878 | vs, sp | 2871 | vs, sp | 2853 | vs | t | v ₅ |
| 2858 | m, C | | | 2860 | s | | | 2865 | s, sh | t | v ₂₂ |
| | | | | | | | | 2830 | sh | | |
| | | | | 2752 | w, sp | 2741 | w, br, sp | 2740 | m | t | 2v ₉ |
| | | | | 2720 | w, sp | 2711 | w, br, sp | 2698 | m | t | v ₈ + v ₁₀ |

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Table I. (Con't.)

| INFRARED | | | | RAMAN | | | | ASSIGNMENT | | | |
|------------------|----------|------------------|-------|------------------|--------|------------------|--------|------------------|------|-----------|----------------------------------|
| GAS | | SOLID | | GAS | | LIQUID | | SOLID | | Conformer | Vibration |
| cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | | |
| | | | | 2665 | w, sp | | | 2650 | m | | |
| | | | | | | | | 2620 | m | | |
| 1618 | s | 1626 | s | | | 1605 | w | 1605 | vw | t | v ₆ |
| 1468 | m, sp, C | 1468 | m, sh | 1469 | m, mp | | | | | t | v ₇ , v ₂₃ |
| 1460 | m, sp, C | 1458 | m, dp | | | 1455 | m, dp | 1457 | m | t | v ₂₄ |
| | | 1451 | m, sh | 1449 | m, mp | | | 1453 | w | t | v ₈ |
| 1375 | s | 1375 | vs | | | 1385 | w, mp | 1387 | vw | t | v ₉ |
| | | | | 1370 | vw, sp | | | | | | |
| | | 1352 | w | | | 1360 | vw, mp | 1353 | vw | t | v ₂₅ |
| 1349 | m, sh, C | 1340 | m | 1343 | vw | 1338 | w, dp | 1342 | w | t | v ₂₆ |
| 1340 | m, sh, C | | | | | | | | | | |
| | | 1256 | w | 1245 | w, sp | 1253 | w, sp | 1253 | w | t | v ₁₀ |
| 1240 | w, br | 1248 | w | 1240 | vw, sp | 1245 | w, mp | | | t | v ₂₇ |
| 1170 | m, C | 1177 | m | 1178 | w, dp | 1175 | m, dp | 1179 | m | t | v ₂₈ |
| | | 1138 | m | | | | | | | | |
| 1129 | w, A | 1132 | s | 1130 | m, sp | 1135 | m, mp | 1138 | w | t | v ₁₁ |
| 1047 | w, C | 1052 | w | | | | | | | | |
| 1029 | w, C | 1036 | m | 1033 | w, sp | 1035 | m, dp | 1039 | s | t | v ₂₉ |
| 976 | m, C | 989 | vs | 970 | vw, br | 981 | w, mp | 991 | vw | t | v ₃₀ |

Table I. (Con't.)

| INFRARED | | | | RAMAN | | | | ASSIGNMENT | | | |
|------------------|------|------------------|------|------------------|------|------------------|------|------------------|------|-----------|--------------|
| GAS | | SOLID | | GAS | | LIQUID | | SOLID | | Conformer | Vibration |
| cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | cm ⁻¹ | Int. | | |
| | | 90 | vw | | | | | | | | Lattice mode |

^aAbbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; t, s-trans; g, gauche; sp, strongly polarized; mp, medium polarized; dp, depolarized; and A, B, C are band contours.

Table II. Vibrational frequencies and assignments for isopropylamine-d₂^a

| INFRARED | | | | RAMAN | | | | | | Conformer | Vibration |
|----------|------|-------|-------|-------|-------|--------|-------|--------------|---------|-----------|---------------------------------|
| Gas | Int. | Solid | Int. | Gas | Int. | Liquid | Int. | Solid | Int. | | |
| 2964 | vs | 2964 | vs,sh | 2968 | vs,sp | 2960 | s,mp | 2969 2957 | s vs | t | v ₂ ,v ₂₀ |
| 2954 | vs | 2950 | vs | | | | | | | t | v ₂₁ |
| | | | | 2942 | vs,sp | | | 2949 | s | t | v ₃ |
| 2924 | m | 2922 | m | 2929 | vs,sp | 2932 | vs,sp | 2932 | vw | g | v ₄ |
| | | | | 2916 | s | 2920 | s,sp | 2919 | vs | t | v ₄ |
| | | | | 2907 | s,sp | 2906 | s,sp | | | t | 2v ₈ |
| 2904 | m,sh | 2890 | m,sh | 2883 | vs,sp | 2867 | vs,sp | 2837 | vs | t | v ₅ |
| | | | | 2876 | vs,sp | | | | | | |
| 2856 | m,C | 2864 | m | | | | | 2865 | s | t | v ₂₂ |
| 2850 | w,sh | 2832 | m | 2852 | s,sp | 2840 | sh,sp | | | t | v ₇ + v ₉ |
| | | 2782 | m | 2765 | m,sp | 2754 | w,sp | 2751 | w | t | 2v ₉ |
| | | | | 2739 | m,sp | 2724 | | 2722 | | | |
| | | | | 2726 | m,sp | | | | | | |
| | | | | 2645 | | 2634 | | 2632 | | | |
| | | | | 2532 | w,mp | 2510 | w,dp | 2495 | s | t | v ₁₉ |
| | | 2491 | s | 2492 | w,sp | | | | | g | v ₁₉ |
| | | | | 2458 | w,sp | | | | | | |
| | | 2358 | m | 2447 | s,sp | 2434 | m,sp | 2360 | s | t | v ₁ |
| | | | | 2421 | w,sp | | | | | | |
| | | | | 2402 | m,sp | 2390 | m,sp | | | g | v ₁ |

Table II. (Con't.)

| INFRARED | | | | RAMAN | | | | | | Conformer | Vibration |
|----------|--------|-------|-------|-------|-----------|--------|-----------|-------|--------|-----------|----------------------|
| Gas | Int. | Solid | Int. | Gas | Int. | Liquid | Int. | Solid | Int. | | |
| 1468 | m, C | 1464 | m, sh | 1469 | m | | | 1470 | vw, sh | t | ν_7, ν_{23} |
| 1459 | s, C | 1452 | m | 1460 | w, mp | 1458 | m, dp | 1459 | s | t | ν_{24} |
| 1450 | sh | 1450 | m, sh | 1449 | w, mp | 1452 | m, sp | 1450 | m | t | ν_8 |
| 1386 | s, A | 1375 | vs | 1388 | vw, sp | 1382 | w, sp | 1383 | m | t | ν_9 |
| 1348 | s, C | 1333 | s | 1345 | w, mp | 1338 | m, dp | 1339 | m | t | ν_{25} |
| 1210 | s, A | 1225 | s | 1210 | vw | 1211 | vw, mp | 1232 | vw | t | ν_{10}, ν_{27} |
| 1206 | m, sh | 1216 | w, sh | | | | | | | | |
| | | 1174 | m | 1187 | w, sp | 1179 | m, sp | 1177 | m | t | ν_6 |
| | | | | 1180 | w, sp | | | | | | |
| 1160 | vw | 1164 | w, sh | 1161 | vw, dp | 1167 | w, sh, dp | 1168 | m | t | ν_{28} |
| | | | | | | 1150 | vw, mp | | | | |
| 1128 | vw, B | 1129 | w | 1128 | vw, sp | | | 1122 | vw, sh | t | ν_{11} |
| | | | | | | 1127 | w, mp | | | | |
| 1118 | vw, C | 1112 | m | 1121 | vw, sh | | | 1116 | vw | | |
| 1077 | vw | 1014 | vw | | | | | | | | ν_{25} |
| 984 | vw, C | 996 | w | | | | | | | t | ν_{29} |
| 957 | m, A | 955 | m | 957 | vw, sp | 955 | w, sp | 957 | m | t | ν_{15} |
| | | 950 | w | 945 | vw, dp | 938 | w, dp | 951 | m | t | ν_{30} |
| 930 | vw, br | 938 | m | 935 | w, sh, sp | | | | | t | ν_{12} |
| 913 | vw, C | 918 | m | 920 | sh | 920 | vw, br | 920 | vw | t | ν_{13} |

Table II. (Con't.)

| INFRARED | | | | RAMAN | | | | | | Conformer | Vibration |
|----------|-------|-------|-------|-------|--------|--------|-----------|-------|------|-----------|------------|
| Gas | Int. | Solid | Int. | Gas | Int. | Liquid | Int. | Solid | Int. | | |
| | | | | | | | | 863 | vw | | |
| 852 | vw | 855 | m | 855 | w, sp | 850 | w, sp | 854 | w | | |
| | | | | 834 | w, sp | | | | | | |
| 801 | w | 802 | s | 803 | s, sp | 804 | s, sp | | | g | ν_{14} |
| | | 811 | w, sh | 788 | s, sp | 792 | s, sp | 807 | s | t | ν_{14} |
| 725 | w | 774 | w | | | | | 751 | vw | | |
| 701 | w, C | 701 | s | 704 | w, sp | | | 708 | w | | |
| | | | | | | 685 | w, br, sp | | | | |
| 673 | w, sh | | | 671 | vw, sp | | | | | | ν_{26} |
| 662 | w, sh | | | 662 | vw, sp | | | | | | |
| 643 | s, A | | | 645 | m, sp | | | | | t | ν_{15} |
| 634 | m | | | 637 | w, sp | | | | | g | ν_{15} |
| 628 | m, sh | 620 | vw | 614 | vw, sp | | | | | | |
| | | 482 | m | | | 468 | sh, sp | | | | |
| | | 465 | w | | | 461 | sh, sp | | | | |
| 454 | m | 470 | m | 453 | vw, sp | 451 | vw, sp | 472 | w | t | ν_{16} |
| 439 | w | | | 439 | w, sp | 446 | w, sp | | | g | ν_{16} |
| 381 | w, A | 406 | m | 382 | vw, sp | 388 | w, mp | 405 | vw | t | ν_{17} |
| 363 | w | 390 | m | 365 | w, mp | 370 | w, mp | 368 | w | t | ν_{31} |
| | | | | | | 260 | vvw | 261 | vw | | |

Table II. (Con't.)

| INFRARED | | | | RAMAN | | | | Conformer | Vibration | | |
|----------|------|-------|------|-------|------|--------|----------|-----------|-----------|-------|--------------|
| Gas | Int. | Solid | Int. | Gas | Int. | Liquid | Int. | | | Solid | Int. |
| 236 | w | 243 | vw | | | | | | | t | ν_{33} |
| 195 | w,C | | | | | | | | | t | ν_{32} |
| 171 | m,C | | | | | 171 | vw,br,mp | | | g | ν_{32} |
| | | 147 | w | | | | | | | | Lattice mode |
| | | 119 | m | | | | | | | | Lattice mode |
| | | 85 | w | | | | | | | | Lattice mode |

^aAbbreviations used: see Table I.

Table III. Frequencies (cm^{-1}) and approximate descriptions
of the normal modes of gaseous isopropylamine

| A' | Description | $(\text{CH}_3)_2\text{CHNH}_2$ | | $(\text{CH}_3)_2\text{CHND}_2$ | |
|------------|--|--------------------------------|---------------|--------------------------------|---------------|
| | | <u>s-trans</u> | <u>gauche</u> | <u>s-trans</u> | <u>gauche</u> |
| ν_1 | NH_2 stretch, symmetric | 3342 | 3328 | 2447 | 2402 |
| ν_2 | CH_3 stretch, antisymmetric, in-plane, in phase | 2968 | | 2968 | |
| ν_3 | CH_3 stretch, antisymmetric, out-of-plane, in phase | 2945 | | 2942 | |
| ν_4 | CH stretch, symmetric | 2932 | 2918 | 2916 | 2929 |
| ν_5 | CH_3 stretch, symmetric, in phase | 2878 | | 2883 | |
| ν_6 | NH_2 scissor | 1618 | | 1187 | |
| ν_7 | CH_3 deformation, antisymmetric, in-plane, in phase | 1469 | | 1469 | |
| ν_8 | CH_3 deformation, antisymmetric, out-of-plane, in phase | 1449 | | 1449 | |
| ν_9 | CH_3 deformation, symmetric, in phase | 1375 | | 1388 | |
| ν_{10} | CH deformation, in-plane | 1245 | | 1206 | |
| ν_{11} | CH_3 rock, in-plane, in phase | 1130 | | 1128 | |
| ν_{12} | CH_3 rock, out-of-plane, in phase | 942 ^a | | 935 | |
| ν_{13} | C-C stretch, symmetric | 919 ^a | | 913 | |
| ν_{14} | C-N stretch | 819 | 826 | 788 | 803 |
| ν_{15} | NH_2 wag | 785 | 781 | 643 | 673 |
| ν_{16} | C-C-N deformation, in-plane | 472 | 459 | 454 | 439 |
| ν_{17} | C-C-C deformation, symmetric | 404 | 407 | | 381 |
| ν_{18} | CH_3 torsion, in-plane | 258 | | -- | |
| A'' | | | | | |
| ν_{19} | NH_2 stretch, antisymmetric | 3411 | 3393 | 2532 | 2492 |
| ν_{20} | CH_3 stretch, antisymmetric, in-plane, in phase | 2965 | | 2964 | |

Table III. (Con't.)

| A'' | Description | $(\text{CH}_3)_2\text{CHNH}_2$ | | $(\text{CH}_3)_2\text{CHND}_2$ | |
|------------|--|--------------------------------|-------------------|--------------------------------|-------------------|
| | | <u>s-trans</u> | <u>gauche</u> | <u>s-trans</u> | <u>gauche</u> |
| ν_{21} | CH_3 stretch, antisymmetric, out-of-plane, out-of-phase | | 2950 | | 2954 |
| ν_{22} | CH_3 stretch, symmetric, out-of-phase | | 2860 | | 2856 |
| ν_{23} | CH_3 deformation, antisymmetric, in-plane out-of-phase | | 1469 | | 1469 |
| ν_{24} | CH_3 deformation, antisymmetric, out-of-phase, | | 1460 | | 1459 |
| ν_{25} | NH_2 twist | | 1360 ^a | | 1014 ^b |
| ν_{26} | CH_3 deformation, symmetric, out-of-phase | | 1343 | | 1345 |
| ν_{27} | CH deformation, out-of-plane | | 1240 | | 1210 |
| ν_{28} | C-C rock, out-of-plane, out-of-phase | | 1178 | | 1161 |
| ν_{29} | CH_3 rock, in-plane, out-of-phase | | 1029 | | 984 |
| ν_{30} | CH_3 rock, in-plane, out-of-phase | | 976 | | 945 |
| ν_{31} | C-C-N deformation, out-of-plane | | 369 | | 363 |
| ν_{32} | NH_2 torsion | 267 | | 221 | 195 |
| ν_{33} | CH_3 torsion, out-of-phase | | 236 | | 236 |

(a) Frequency from the liquid phase.

(b) Frequency from the solid phase.

Table IV. Observed bands (cm^{-1}) and proposed assignments of the vibrational spectrum of gaseous isopropylamine- d_0 below 520 cm^{-1}

| RAMAN | | INFRARED | | | ASSIGNMENT ^a | | Observed | |
|------------------|------------------------------------|------------------|------------------------------------|-----|-------------------------|--------------------------------|-----------------------|------|
| cm^{-1} | Relative ^a Intensity | cm^{-1} | Relative ^a Intensity | | | Calculated cm^{-1} | | |
| 512.0 | w | 512.1 | w | t | 02 \leftarrow 00 | 258.2 + 253.1 = 511.3 | 0.3 | |
| | | 504.3 | w | t | 03 \leftarrow 01 | 253.1 + 251.2 = 504.3 | -0.8 | |
| | | 497.1 | | vw | t | 04 \leftarrow 02 | | 0.1 |
| | | 490.2 | | vw | | | | |
| | | 488.4 | | vw | | | | |
| 485.0 | vw | 484.7 | w | | | | | |
| | | 482.0 | | vw | | | | |
| | | 476.0 | | vvw | | | | |
| 472.0 | vs | 471.5 | vs | t | ν_{16} | | | |
| 468.0 | w,sh | 469.1 | m | t | 20 \leftarrow 00 | 236.1 + 233.0 = 469.0 | 0.0 | |
| | | 464.8 | | vw | t | 30 \leftarrow 10 | 233.0 + 230.7 = 463.7 | 0.7 |
| 460.2 | s | 459.4 | m | g | ν_{16} | | | |
| 455.0 | vw | 455.0 | | vvw | | | | |
| | | 446.3 | | vvw | | | | |
| | | 442.7 | | vvw | | | | |
| 406.2 | m | 407.0 | w | g | ν_{17} | | | |
| | | 404.0 | | m | t | ν_{17} | | |
| | | 370.1 | | vvw | | | | |
| 368.0 | w | 369.0 | | vw | t | ν_{31} | | |
| | | 269.0 | | vvw | | | | |
| | | 266.9 | | m | t | 1 \leftarrow 0 | ν_{32} | 0.0 |
| | | 264.4 | | m | t | 2 \leftarrow 1 | | 0.0 |
| | | 258.2 | | w | t | 01 \leftarrow 00 | ν_{18} | 0.9 |
| | | 253.1 | | w | t | 02 \leftarrow 01 | | -1.4 |
| | | 251.2 | | w | t | 03 \leftarrow 02 | | 0.5 |
| | | 246.0 | | w | t | 3 \leftarrow 2 | | 0.0 |

Table IV. (Con't.)

| RAMAN | | INFRARED | | ASSIGNMENT ^a | | Observed Calculated | |
|------------------|------------------------------------|------------------|------------------------------------|-------------------------|--|------------------------|------------|
| cm ⁻¹ | Relative ^a Intensity | cm ⁻¹ | Relative ^a Intensity | | | cm ⁻¹ | |
| 236.0 | vw | 236.1 | s | t | 10 ⁺ 00 | v ₃₃ | 1.1 |
| | | 233.0 | m | t | 20 ⁺ 10 | | -1.1 |
| | | 230.7 | w | t | 30 ⁺ 20 | | 0.7 |
| | | 223.0 | vw | t | 11 ⁺ 01 | | -1.3 |
| 221.3 | w | 220.5 | vs | g | 1 [±] 0 [±] | v ₃₂ | 0.1 |
| | | 211.0 | s | g | 2 ⁻ +1 ⁺ 3 ⁻ +2 ⁺ | | 0.3 0.0 |
| | | 207.7 | m | g | 2 ⁺ +1 ⁻ | | -0.5 |
| | | 197.0 | m | | | | |
| | | 195.1 | m | | | | |
| | | 186.2 | m | g | 3 ⁺ +2 ⁻ | | 0.1 |
| | | 180.2 | w | | | | |
| | | 176.0 | w | | | | |
| | | 165.9 | vw | | | | |
| | | 123.2 | vw | | | | |

^aAbbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; t, s-trans; g, gauche.

Table V. Observed bands (cm^{-1}) and proposed assignments of the vibrational spectrum of gaseous isopropylamine- d_2 below 520 cm^{-1}

| RAMAN | | INFRARED | | ASSIGNMENT ^a | | Observed Calculated |
|------------------|------------------------------------|------------------|------------------------------------|-------------------------|------------------------------------|------------------------|
| cm^{-1} | Relative Intensity ^a | cm^{-1} | Relative Intensity ^a | | | cm^{-1} |
| | | 503.7 | w | | | |
| | | 501.2 | vw | | | |
| | | 496.8 | vw | | | |
| 465.0 | m | 465.3 | m | | | |
| | | 461.6 | m | | Methyl torsions | |
| 460.0 | w | 459.5 | m | | | |
| | | 457.5 | vvw | | | |
| 456.5 | vw | 456.2 | s | | | |
| 453.0 | w | 453.8 | vs | t | ν_{16} | |
| | | 452.5 | w | | | |
| | | 451.3 | m | | | |
| | | 449.5 | w | | | |
| | | 448.0 | vvw | | | |
| | | 447.0 | vvw | | | |
| 445.0 | sh | | | | | |
| 439.2 | vs | 439.0 | vw | g | ν_{16} | |
| | | 436.0 | vw | | | |
| 432.5 | vw | 434.0 | w | | | |
| 405.0 | w | 405.0 | vw | | | |
| | | 391.5 | vvw | | | |
| 384.0 | w,sh | 385.6 | vw | t | 2 \times 0 194.8 + 189.4 = 384.2 | 5.6 ^b |
| 382.0 | m | 382.3 | vw | g | ν_{17} | |
| | | 380.8 | m | t | ν_{17} | |
| 378.0 | w | 378.5 | w | t | 1st hot band of 380.8 | |

Table V. (Con't.)

| RAMAN | | INFRARED | | | ASSIGNMENT | Observed Calculated |
|------------------|------------------------------------|------------------|------------------------------------|---|---|------------------------|
| cm ⁻¹ | Relative ^a Intensity | cm ⁻¹ | Relative ^a Intensity | | | cm ⁻¹ |
| 374.0 | | 375.5 | w | t | 2nd hot band of 380.8 | |
| 365.0 | w | 363.0 | vw | t | ν_{31} | |
| 362.0 | w,sh | 361.1 | vw | t | 3 \leftarrow 1 189.4 + 171.5 = 360.9 | -0.8 ^b |
| | | 353.5 | vvw | | | |
| | | 349.3 | vvw | | | |
| | | 330.9 | w | t | 4 \leftarrow 2 171.5 + 158.6 = 330.1 | -7.7 ^b |
| 328.0 | vw | 328.3 | vvw | g | 2 \leftarrow 0 \pm 170.7 + 157.5 = 328.2 | 0.0 ^b |
| | | 306.2 | w | t | 5 \leftarrow 3 | 1.7 |
| 300.0 | vw | 299.0 | vvw | g | 3 \leftarrow 1 \leftarrow 157.5 + 141.8 = 299.3 | -1.5 ^b |
| | | 297.2 | vvw | g | 3 \leftarrow 1 \leftarrow 157.5 + 138.5 = 296.0 | 2.0 ^b |
| | | 266.0 | vvw | | | |
| | | 258.2 | vvw | | | |
| | | 252.0 | vvw | | | |
| | | 245.2 | vw | | | |
| | | 242.4 | vw | | | |
| | | 235.8 | w | | | |
| | | 232.6 | w | | | |
| | | 228.2 | w | | Methyl torsions | |
| | | 224.2 | vw | | | |
| | | 222.2 | vw | | | |
| | | 220.2 | vw | | | |
| | | 214.5 | vvw | | | |
| | | 211.4 | vvw | | | |
| | | 207.5 | vvw | | | |
| | | 196.0 | vvw | | | |

Table V. (Con't.)

| RAMAN | | INFRARED | | ASSIGNMENT | | Observed Calculated | |
|------------------|------------------------------------|------------------|------------------------------------|------------|--------------------------------|------------------------|------|
| cm ⁻¹ | Relative ^a Intensity | cm ⁻¹ | Relative ^a Intensity | | | cm ⁻¹ | |
| | | 194.8 | m | t | 1←0 | ν_{32} | 0.8 |
| | | 189.4 | m | t | 2←1 | | 3.4 |
| | | 179.6 | w | | | | |
| | | 177.1 | w | | | | |
| | | 173.0 | vw | | | | |
| | | 171.7 | m, sh | t | 3←2 | | -4.0 |
| 173.0 | m | 170.7 | vs | g | 1±←0± | ν_{32} | 0.0 |
| 168.0 | w | 168.4 | w | | | | |
| | | 160.0 | w | | | | |
| | | 158.6 | m | t | 4←3 | | -3.5 |
| 159.0 | w | 157.5 | s | g | 2±←1± | | -0.2 |
| 145.0 | w | 143.5 | w | | | | |
| | | 142.5 | vw | | | | |
| | | 141.8 | w | g | 3 ⁻ ←2 ⁺ | | -2.3 |
| | | 140.0 | vw | | | | |
| | | 138.5 | vw | g | 3 ⁺ ←2 ⁻ | | 1.1 |
| | | 127.5 | vvw | | | | |
| | | 123.5 | vvw | | | | |

^aAbbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; t, s-trans; g, gauche.

^bTransition not used in fitting potential function.

Table VI. Potential coefficients for the amino torsions of
isopropylamine-d₀ and isopropylamine-d₂ in cm⁻¹

| Coefficient | Isopropylamine-d ₀ ^a | | Isopropylamine-d ₂ ^b | |
|----------------|--|------------|--|------------|
| | Value | Dispersion | Value | Dispersion |
| V ₁ | 65.0 | 1.9 | 30.8 | 14.5 |
| V ₂ | 30.0 | 2.2 | 187.6 | 23.5 |
| V ₃ | 978.9 | 1.3 | 863.1 | 5.4 |
| V ₄ | 228.1 | 1.9 | 84.5 | 17.0 |
| V ₅ | -25.3 | 0.8 | -43.2 | 6.6 |
| V ₆ | -143.3 | 1.1 | -27.1 | 4.6 |
| ΔH | 156.0 | -- | 183.0 | -- |

^aCalculated using $F_0 = 9.762$, $F_1 = 0.040$, $F_2 = 0.047$ and nine frequencies.

^bCalculated using $F_0 = 5.126$, $F_1 = 0.038$, $F_2 = -0.038$ and eleven frequencies.

Table VII. Potential coefficients for the methyl torsions of s-trans isopropylamine-d₀, with calculated dispersions σ is the standard deviation of the frequency fit, calculated fitting 12 transitions

| Coefficient | Value (cm ⁻¹) | Dispersion |
|-------------------|------------------------------|------------|
| $V_{30} = V_{03}$ | 1677.8 | 18.2 |
| $V_{60} = V_{06}$ | -52.6 | 6.7 |
| V_{33} | 198.1 | 31.0 |
| V'_{33} | -102.4 | 4.3 |
| $V_{30} - V_{33}$ | 1479.7 | 20.7 |
| $g^{44} = g^{55}$ | | 11.115 |
| g^{45} | | -0.251 |
| σ | | 1.05 |

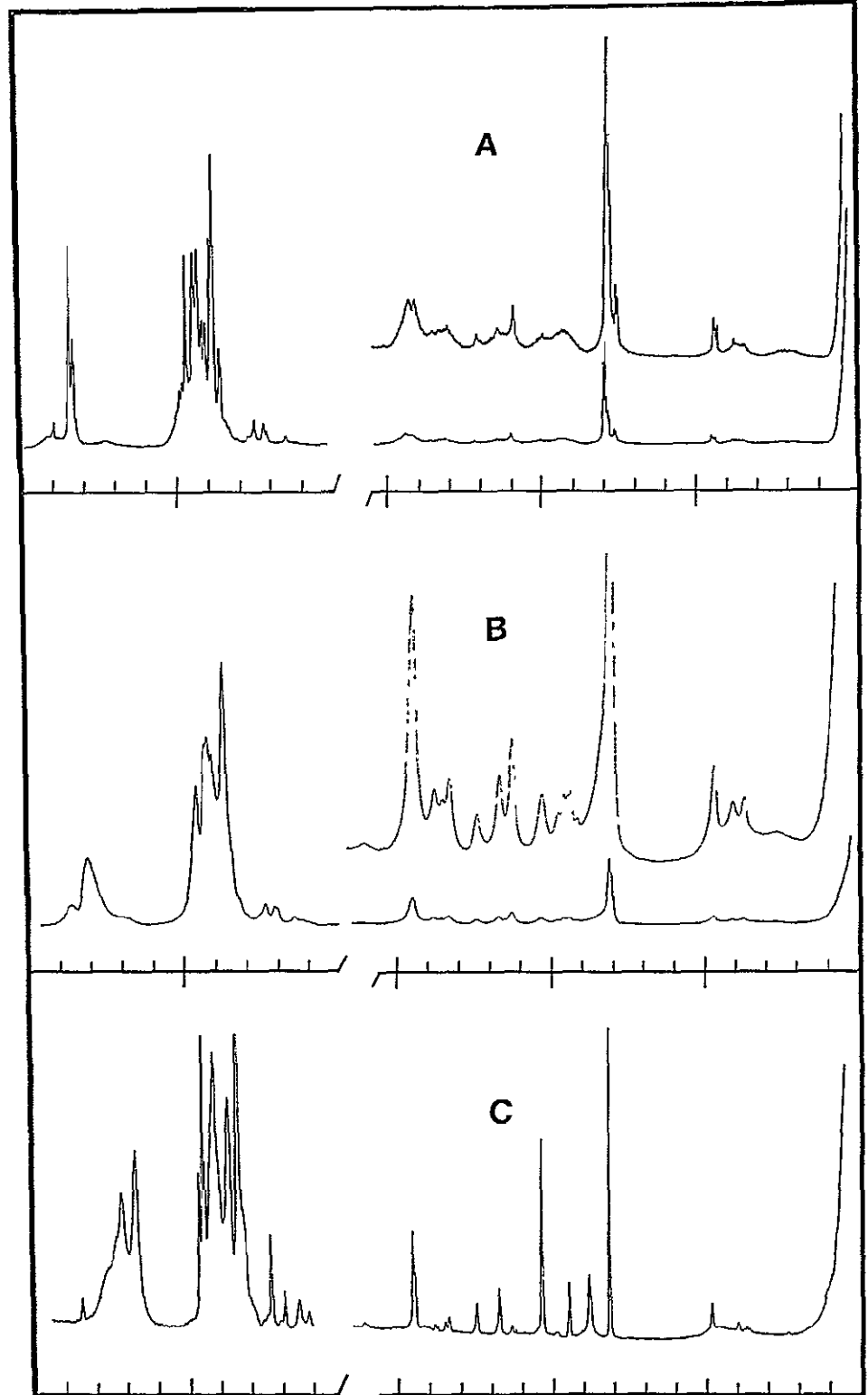
Table VIII. Calculated values for the gaseous-phase thermodynamic functions^a,
in units of $\text{J}\cdot\text{K}^{-1}\text{ mol}^{-1}$, and mole fraction of the high energy
gauche conformer of isopropylamine- d_0

| T | $-(G^\ominus - H^\ominus_0)/T$ | $(H - H^\ominus_0)/T$ | S^\ominus | C^\ominus_P | X_g |
|--------|--------------------------------|-----------------------|-------------|---------------|-------|
| 273.15 | 245.2 | 58.4 | 303.6 | 89.5 | 0.459 |
| 298.15 | 250.6 | 61.2 | 311.8 | 95.8 | 0.473 |
| 300.0 | 251.0 | 61.4 | 312.4 | 96.3 | 0.474 |
| 400.0 | 270.6 | 73.3 | 343.9 | 121.7 | 0.513 |
| 500.0 | 288.4 | 85.3 | 373.7 | 144.6 | 0.536 |
| 600.0 | 305.1 | 96.8 | 401.9 | 163.8 | 0.551 |
| 700.0 | 320.9 | 107.6 | 428.4 | 179.9 | 0.560 |
| 800.0 | 336.0 | 117.5 | 453.4 | 193.5 | 0.569 |
| 900.0 | 350.4 | 126.6 | 477.0 | 205.3 | 0.575 |
| 1000.0 | 364.2 | 134.9 | 499.2 | 215.6 | 0.580 |

^aCalculated using a value of 1749 J mol^{-1} (418 cal mol^{-1}) for ΔH^\ominus_0

FIGURE CAPTIONS

- Figure 1. Raman spectra of isopropylamine- d_0 : (A) gas; (B) liquid; (C) solid.
- Figure 2. Raman spectra of isopropylamine- d_2 : (A) gas; (B) liquid; (C) solid.
- Figure 3. Mid-infrared spectra of isopropylamine- d_0 : (A) gas; (B) solid.
- Figure 4. Mid-infrared spectra of isopropylamine- d_2 : (A) gas; (B) solid.
- Figure 5. Far infrared spectra of gaseous isopropylamine- d_0 (A), and isopropylamine- d_2 (B), from 500 to 80 cm^{-1} . Spectra A and B were recorded using a 6.25 micron beamsplitter and sample pressures of approximately 30 torr.
- Figure 6. Asymmetric potential function for the internal rotation about the C-N bond in isopropylamine- d_0 , including the observed energy levels. The dihedral angle of zero corresponds to the s-trans conformer.



3500 3000 1500 1000 500 0

WAVENUMBER (CM^{-1})

