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Raman, infrared and microwave spectra, r_0 structural parameters, and conformational stability of isopropylisocyanate

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ABSTRACT: The microwave spectrum of isopropylisocyanate, $(\text{CH}_3)_2\text{CHNCO}$, has been investigated from 11,000 to 21,000 MHz and 18 transitions for the more stable *trans* conformer were assigned and $A=6693.23(15)$, $B=2263.10(3)$, $C=1960.05(2)$ MHz were obtained. By utilizing these rotational constants along with ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained for the *trans* conformer along with estimated values for the *gauche* conformer. Variable temperature Raman and infrared spectra of xenon solutions have been recorded and a ΔH value of $115 \pm 11 \text{ cm}^{-1}$ ($1.38 \pm 0.13 \text{ kJ/mol}$) has been determined. The conformational stabilities have been predicted from ab initio calculations utilizing several different basis sets up to cc-PVQZ for MP2(full) and 6-311+G(3df,3pd) for density functional theory calculations by the B3LYP method. From the MP2(full)/cc-PVQZ calculations an energy difference of 87 cm^{-1} (1.04 kJ/mol) is predicted between the *trans* and the *gauche* forms and 168 cm^{-1} (2.01 kJ/mol) for the *cis* form which is a transition state.

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^b Taken in part from the dissertation of B. S. Deodhar, which will be submitted in partial fulfillment for the Ph.D.

INTRODUCTION

The substitution of isocyanate (NCO) or isothiocyanate (NCS) for the hydrogen atom on simple hydrocarbons has resulted in a number of small molecules where there has been considerable controversy regarding the most stable conformation or conformations. There have been frequent discrepancies observed amongst the experimental conformational determinations from microwave spectra, vibrational spectra, and electron diffraction studies[1-3]. More recently, predicted structures have been reported [4-5] from ab initio calculations, which do not agree in some cases with the experimentally determined structures. These originate from several factors with the most significant one from the large CNC angles which may become linear with very few vibrations or the potential well may be so shallow that it cannot accommodate a single vibrational state. Also, the low frequency large amplitude vibrations can result where a large number of molecules are linear in the vibrational excited states at ambient temperature which makes it difficult to determine the structure of the ground vibrational state. Initially, we began the study of several small hydrocarbons with monosubstituted NCO and NCS groups to determine their conformational stabilities, the enthalpy differences between or among the conformers, and their structural parameters. For example, one of the recent molecules we investigated was cyclopropylisocyanate, *c*-C₃H₅NCO, where the two stable conformers were clearly determined to be the *trans* and *cis* conformers with the *trans* form the more stable conformer with an enthalpy difference of $77 \pm 8 \text{ cm}^{-1}$ ($0.92 \pm 0.10 \text{ kJ/mol}$). This result showed conclusively that the earlier ab initio prediction⁴ from which reported that two *gauche* conformers with dihedral C=NC_αC angles of 144.9° and 324.3° relative to the two carbon atoms in the ring was undoubtedly wrong. Similarly, from the fact that the centrifugal distortion constants could not be obtained from the simple quadratic equation it was then possibly taken [6] to indicate that the second conformer may not be the *cis* form. However, this failure is due to the

large amplitude vibration which must be governed by a potential function frequently referred to as a “champagne bottle” potential function where the origin of the coordinate system is at the critical point on top of the potential hump [7].

As a continuation of these studies we have investigated the conformational stabilities of isopropylisocyanate and recorded the FT-microwave spectra to determine the structural parameters. In an earlier microwave study [8] of isopropylisocyanate the individual lines could not be assigned but the low resolution spectrum provided the value for the sum of the $B + C$ rotational constants. By using reasonable structural parameters for their values a good agreement for the *skew* form was obtained which was significantly different from the predicted $B + C$ values for the *trans*, *gauche*, and *cis* forms (Fig. 1). Similar conformational data for this molecule was also obtained from an electron diffraction study [9] with the conclusion from both structural studies that there was only one form present. Also from the vibrational study, it was concluded that there was primarily one conformer present since none of the skeletal modes which should be the most sensitive for conformer determination exhibited any doubling of frequencies in the fluid phases. Also, the lack of any bands observed in the infrared spectrum of the gas which disappeared in the infrared spectrum of the solid was further taken as an indication that there was predominant evidence for mainly only one conformer present.

From our more recent studies of organoisocyanates molecules this single conformer conclusion is expected to be in error. Therefore, the microwave spectrum has been re-investigated by a FT-microwave instrument at 4° K at low frequencies so individual lines could be assigned as well as a search could be made for a second conformer. In addition to the microwave studies we have investigated the variable temperature Raman and far infrared spectra of xenon solutions with the expectation of identifying vibrations of a second conformer. To

support these experimental studies we have carried out MP2(full) ab initio and density functional theory (DFT) calculations by the B3LYP method by utilizing a variety of basis sets. The results of these spectroscopic, structural, and theoretical studies of isopropylisocyanate are reported herein.

EXPERIMENTAL METHODS

The isopropylisocyanate sample was purchased from Aldrich, St. Louis, MO with a stated purity of 99% and it was utilized without further purification.

The microwave spectra of isopropylisocyanate were recorded using a “mini-cavity” Fourier-transform microwave spectrometer [10-11] at Kent State University. The isopropylisocyanate sample was entrained in 70:30 Ne-He carrier gas mixture at 2 atm and expanded into the cavity using a reservoir nozzle [11] made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange, external to the vacuum chamber, and the expansion passes through a 0.182-inch diameter hole into the resonant cavity. The center of the expansion is offset from the center of the mirror by 1 inch.

The sample was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer and details of the irradiation and heterodyne detection circuitry can be found in Ref.10. The vacuum system can accommodate pulse repetition rates of up to 15 s⁻¹ while maintaining a pressure below 10⁻⁴ torr, and the instrument can scan 450 MHz in 6 hours while averaging 100 shots per scan segment. The frequencies for the measured transitions in the region of 12,000 to 19,000 MHz for the *trans* conformer of isopropylisocyanate are listed in Table I along with their assignments. Also listed are the frequency differences between the measured values and the values obtained from the determined rotational constants and the

centrifugal distortion constants (Table II).

The mid-infrared spectrum of the gas (Figs. 2(a) and 3(a)) and solid were obtained from 3500 to 220 cm^{-1} on a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectra of the gas and solid were obtained with a theoretical resolution of 0.5 cm^{-1} for the gas and 2 cm^{-1} for the solid with 128 interferograms added and truncated. It needs to be noted that annealing was attempted multiple times with reduction in some band intensities in the spectra however a single crystal could not be obtained.

The mid-infrared spectra of isopropylisocyanate dissolved in liquefied xenon (Fig. 4(b)) were recorded on a Bruker model IFS-66 Fourier interferometer equipped with a Globar source, Ge/KBr beamsplitter and DTGS detector. The interferograms were recorded at variable temperatures ranging from -55 to -100°C with 100 scans and transformed by a Blackman-Harris apodization function with a theoretical resolution of 1.0 cm^{-1} . The temperature studies in liquefied xenon were carried out in a specially designed cryostat cell, which is composed of a copper cell with a 4 cm path length and wedged silicon windows sealed to the cell with indium gaskets. The temperature was monitored by two platinum thermoresistors and the cell was cooled by the vapors from boiling liquid nitrogen. All of the observed fundamental modes for the *trans* and *gauche* conformers in the infrared and Raman spectra are listed in Tables III and IV, respectively.

The low frequency and far infrared spectra (60 to 600 cm^{-1}) of the sample dissolved in liquid xenon were recorded on a Bruker model IFS-66 v/S Fourier transform spectrophotometer equipped with a Globar source, a 6.0 μm Mylar beamsplitter, and a liquid helium cooled Si bolometer. The sample was contained in a 7 cm cell fitted with Si Windows and the sample

added as described for the mid-infrared studies. For all spectra, 250 interferograms were collected at 0.5 cm^{-1} resolution, averaged and transformed with a Blackman-Harris three term function.

Raman spectra were recorded using a Trivista 557 spectrometer consisting of a double $f = 50\text{ cm}$ monochromator equipped with a $2000\text{ lines mm}^{-1}$ grating, a $f = 70\text{ cm}$ spectrograph equipped with a $2400\text{ lines mm}^{-1}$ grating, and a back-illuminated LN2-cooled PI Acton Spec-10:2 kB/LN 2048×512 pixel CCD detector. For all experiments, the 514.5 nm line of a 2017-Ar S/N 1665 Spectra-Physics argon ion laser was used for Raman excitation, with the power set to 0.8 Watt . Signals related to the plasma lines were removed by using an interference filter. The frequencies were calibrated by using Neon emission lines, and depending on the set-up used, are expected to be accurate within 0.4 cm^{-1} . The experimental set-up used to investigate the solutions has been described [12-13]. A home-built liquid cell equipped with four quartz windows at right angles was used to record the spectra (Fig. 5).

AB INITIO CALCULATIONS

The LCAO-MO-SCF calculations were performed with the Gaussian-03 program[14] by using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by simultaneous relaxation of all geometric parameters consistent with symmetry restrictions using the gradient method of Pulay[15]. A number of basis sets starting from 6-31G(d), and increasing to 6-311+G(3df,3pd), were employed at the level of Møller-Plesset perturbation theory [16] to second order (MP2), as well as hybrid density functional theory by the B3LYP method, to obtain energy differences (Table V) among the four most likely conformers of isopropylisocyanate. At all levels of calculation carried out, with and without

diffuse functions, predicted conformational stabilities varied extensively with the size of the basis set.

To aid in making the vibrational assignment (Tables III and IV), we have carried out a normal coordinate analysis by utilizing the force fields obtained from the Gaussian-03 program at the MP2(full)/6-31G(d) level. The internal coordinates used to calculate the **G** and **B** matrices for isopropylisocyanate are listed along with the structural parameters in Table VI. By using the **B** matrix, the force field in Cartesian coordinates was converted to a force field in internal coordinates [17]. Subsequently, scaling factors of 0.88 for the CH stretches and 0.90 for all other modes were used, along with the geometric average of scaling factors for interaction force constants, to obtain the fixed scaled force fields and the resultant wavenumbers (Tables III and IV). A set of symmetry coordinates (Supplemental Table 2S) was used to determine the corresponding potential energy distributions (P.E.D.s). The observed and calculated wavenumbers of isopropylisocyanate along with the calculated infrared intensities, Raman activities, depolarization ratios, and P.E.D.s are given in Tables III and IV.

To aid in the identification of the fundamental vibrations for possible conformers of isopropylisocyanate, the infrared and Raman spectrum have been simulated (Figs. 2, 3 and 5, respectively) from the scaled ab initio MP2(full)/6-31G(d) calculation. Infrared intensities were calculated based on the dipole moment derivatives with respect to Cartesian coordinates and transformed into normal coordinate [18]. The evaluation of Raman activity by using the analytical gradient method has been developed [19-20]. The activity S_j can be expressed as: $S_j = g_j (45 \alpha_j^2 + 7 \beta_j^2)$, where g_j is the degeneracy of the vibrational mode j , α_j is the derivative of the isotropic polarizability, and β_j is the anisotropic polarizability. The Raman scattering cross sections, $\partial\sigma_j/\partial\Omega$, which are proportional to Raman activities, can be calculated [21-22] from the

scattering activities as well as the predicted wavenumbers for each normal mode.

MICROWAVE RESULTS

Since the previous spectroscopic studies indicated that at ambient temperature there was predominately a single conformer present for isopropylisocyanate, it was important to determine which of the four possible conformers was the one giving rise to the observed microwave spectra. With this determination, it should be possible to provide a confident vibrational assignment that should provide sufficient information to identify the second conformer if it was present. Thus, the first task was to assign the microwave spectrum.

To assign the microwave spectrum, preliminary rotational constants were predicted for the *trans*, *gauche*, *skew* and *cis* conformer from MP2(full)/6-311G(d,p) calculations and the A, B and C values are listed in Table II for the two most stable conformers. The previously reported [8] B+C MHz average value was 4031 MHz which is smaller than the ab initio predicted value of 4254 MHz for the *trans* form but closer to the value of 3978 MHz predicted for the *skew* form. However, there was a much weaker series neglected that had a spacing of approximately ~4300 MHz which was closer to the predicted value for the *trans* form (Fig. 6). Assignments were then made for several transitions from which A, B and C constants were obtained. The dipole moment components were predicted to be $|\mu_a| = 3.430$ D, $|\mu_b| = 0$, and $|\mu_c| = 0.297$ D so the A-type transitions were expected to dominate with the C-type transitions difficult to identify. The bands were quite difficult to assign and only three “J” transitions with the quadrupole splitting were assigned which could be fitted without the centrifugal distortion values. However, this is expected since a potential function consistent with the “champagne bottle” model is needed to fit transitions with higher frequencies particularly those with larger K values.

By utilizing the assigned transitions listed in Table I, the rotational constants listed in Table II were obtained with uncertainties to the hundredth MHz for the values B and C constants and to a tenth MHz for the A constant. The quadrupole coupling constants were also obtained from these data which are compared to those obtained from the MP2 and B3LYP calculations (Table II).

STRUCTURAL PARAMETERS

In the earlier microwave study, the estimated B+C values for the four possible conformers was obtained by taking the structural parameters for the isopropyl moiety from those reported [23] for isopropylchloride. For the isocyanate group, the structural parameters were estimated from an electron diffraction study [24] of methylisocyanate with an elongation of the C α -N distance by 0.02 Å due to replacement of the two hydrogen atoms with methyl groups (Table VI). The C-N=C angle was varied from 138 to 147° for the various conformers. In the present study, some parameters have to be assumed since there are only three values of the rotational constants. We [25] have shown that ab initio MP2(full)/6-311+G(d,p) calculations predict the r_0 structural parameters for more than fifty carbon-hydrogen distances for substituted hydrocarbons to at least 0.002 Å compared to the experimentally determined values from isolated CH stretching frequencies which were compared [26] to previously determined values from microwave studies. Therefore, all of the carbon-hydrogen distances can be taken from the MP2(full)/6-311+G(d,p) predicted values for both the *trans* and *gauche* conformers of isopropylisocyanate. Also, it has been shown that triple bond distances are nearly constant irrespective of the substitution on it [27] and the C=O of the NCO group behaves similarly to a triple bond. Additionally, there have been several determinations of the N=C(O) bond for a

variety of molecules and it has been found to be approximately the average of the predicted value from the MP2 and B3LYP calculations with the 6-311+G(d,p) basis set and this value was used as the predicted value to start the adjustment. Finally, we fixed the angle N=C=O at the predicted value of 172.6° from the MP2(full)/6-311+G(d,p) calculation. We then adjusted the five remaining heavy atom parameters by utilizing the predicted values from the MP2(full)/6-311+G(d,p) calculation and then minimized the difference between the rotational constants obtained from the adjusted r_0 parameters and the experimental determined values. The determined parameters are listed in Table VI along with estimated values for the *gauche* conformer where the same difference from the adjusted parameters of the *trans* conformer were applied to the *gauche* form. The rotational constants from the adjusted r_0 parameters of the *trans* conformer have differences of 0.06, 0.89, and 0.10 MHz for the A, B, and C constants, respectively.

VIBRATIONAL ASSIGNMENT

In order to obtain the enthalpy difference between the two conformers it is necessary to obtain confident vibrational assignments for the most stable conformer as well as many of the fundamental modes of the second conformer particularly in the “finger print” spectral region where the conformer pairs are best suited for the enthalpy determination. The conclusion that there was only one form present was supported by the electron diffraction results [9] and the low resolution microwave studies [8] which were interpreted to indicate the *skew* form. Nevertheless, there were some evidences for a second conformer since two of the vibrational modes at 767 and 650 cm^{-1} in the spectrum of the gas were reported to have low frequency shoulders but none of the depolarized Raman lines had corresponding bands in the Raman spectrum of the gas, so the

earlier reported vibrational assignment [8] was made on the basis of the molecule having a “pseudo” plane of symmetry. It was assumed that this “local” C_s symmetry was due to the C-N=C angle approaching linearity or forming a very low barrier for the asymmetric torsion so the assignment was made for 19 A' + 14 A'' modes. Therefore, it is expected that this assignment will be very similar to the one which we have made for the most stable *trans* form.

The assignment for most of the fundamentals for the isopropyl moiety could be made from well known “group frequencies” except for some of the lower frequency CH_3 bending modes which are extensively mixed with the heavy atom motions. Similarly, the frequencies for the NCO fundamentals are well known but because of the large amplitude motions of NCO group these vibrations give rise to extensively broad bands without any contours which can be used to distinguish the B-contours of the out-of-plane vibrations. Therefore, considerable reliance was placed on the ab initio predicted fundamental frequencies for distinguishing between the two conformers. Additionally, the predicted intensities of the infrared bands were quite helpful along with some of the predicted depolarization values for the Raman data as well as the activity. However, the most useful information for assigning the fundamentals for the second conformer was the data (Fig. 4(b)) from the xenon solutions.

Since the previous vibrational assignment has been made for a single conformer (*skew*), it is expected to be similar to the assignments made for the *trans* conformer. However, some of these fundamentals have been re-assigned for the *gauche* conformer in the infrared spectrum of the solid i.e. peaks at 1355, 1344, 1325, and 456 cm^{-1} . The band at 1355 cm^{-1} was previously assigned as a combination band ($\nu_{18} + \nu_{27}$) of 257 and 1134 cm^{-1} , respectively, but it is now assigned to the *gauche* form as ν_{15} , which is the CH out-of-plane bend. The previously listed band at 459 cm^{-1} was unassigned but this band at 456 cm^{-1} is now assigned as a *gauche*

fundamental for the CC_2 wag. The CC_2 wag fundamental was predicted to be separated by 22 cm^{-1} between the *trans* (478 cm^{-1}) and *gauche* (456 cm^{-1}) conformer and, as predicted, two bands are observed at 477 and 456 cm^{-1} . Some of the bands currently observed in the infrared spectrum of the solid for the *gauche* form that were not utilized at all in the previous assignment included bands at 1419 , 1130 , 1119 , 907 and 417 cm^{-1} . The 1419 cm^{-1} (ν_{13} , CH_3 symmetric deformation) and 1119 cm^{-1} (ν_{19} , CC_2 antisymmetric stretch) was clearly observed in the infrared spectra of the solid unlike the other three bands which appeared as shoulders on the much stronger corresponding *trans* fundamentals. The band at 1130 and 907 cm^{-1} have similar spectral characteristics like that of the 417 cm^{-1} band. In the earlier assignment, only one band was listed at 413 cm^{-1} (CC_2 twist) in the infrared spectrum of the solid, however, this band was observed as a very strong band in the current study at 411 cm^{-1} (*trans*, CC_2 twist) with a prominent shoulder band at 417 cm^{-1} . It is with this band that there is band contour information which supported the conclusion that the *trans* conformer is more stable. The CC_2 twist for both the *trans* and *gauche* form are predicted at $\sim 419\text{ cm}^{-1}$ (CC_2 twist) with *trans* conformer having a B-type band and the *gauche* form an A-type band. In the infrared spectrum of the gas, a very prominent B-type band contour is observed at 408 cm^{-1} . The temperature study clearly showed the 408 cm^{-1} band arose as the most stable conformer where it gives additional support that the *trans* form is the more stable conformer.

CONFORMATIONAL STABILITY

To determine the enthalpy difference between the *trans* and the *gauche* conformers, variable-temperature studies in liquid xenon were carried out. Because only small interactions are expected to occur between the dissolved molecules and the surrounding noble gas atoms [28-

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SUPPLEMENTAL MATERIAL

See Supplementary Material for Table 1S which contains Transitions not utilized for the determination of the rotational constants for isopropylisocyanate and Table 2S which contains symmetry coordinates data for the trans form of this molecule.

structural parameters obtained from the electron diffraction study are due to the large number of the molecules at ambient temperature which have “nearly free” internal rotation of the NCO moiety. Also, it is believed that the one conformer described as the *skew* structure is approximately the average of the *trans* and *gauche* forms which resulted from the “nearly free” rotation of the NCO group.

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agreement is not as good as frequently obtained from this level of calculation. The centrifugal distortion constants were also predicted and a very large difference for Δ_{JK} and Δ_K was obtained between the values from the MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) predicted values. Because of the large amplitude bending motion of the NCO group the centrifugal distortion constants were not expected to have meaningful values.

With the assigned transitions (Table IS) for the $K_a = 3$ and 4 it was hoped that a few of the transitions were for the predicted *gauche* conformer. The $K_a = 3$ lines were predicted in the 10000 to 11866 MHz but none of them could be identified. However, the predicted potential function (Fig. 8) from the MP2(full)/aug-cc-PVDZ calculation indicates a well with a depth of $\sim 50 \text{ cm}^{-1}$ whereas the predicted frequencies of 34 cm^{-1} for the C-N torsion casts doubt whether a second energy level would exist in the well for the *gauche* conformer. This potential also shows why many vibrational modes in the gas phase have very broad non-descript band contours (Fig. 4) with particular note of the vibrational modes of the NCO bends.

The determined heavy atom structural parameters have relatively small uncertainties where small changes of $0.001 \text{ \AA}$ have a pronounced effect on the fit of the rotational constants. Thus, the estimated uncertainties for three of the distances are $\pm 0.003 \text{ \AA}$ with the other two $\pm 0.005 \text{ \AA}$ and $\pm 0.5^\circ$ for the angles. For a comparison of these parameters, the structural parameters from the electron diffraction study [9] are available where it was assumed that there was a single *skew* conformer present. With this assumption, it required the C-NCO angle to have a very large value of $159.0 \pm 3.0^\circ$ which clearly is too large. Two other heavy atom parameters from the electron diffraction study differs significantly from the adjusted r_0 parameters with the $C_4N=C$ angle $132.6 \pm 1.0^\circ$ and $C=O$ distance $1.184 \pm 0.004 \text{ \AA}$ but the other parameters are essentially in agreement with the values obtained in this study. It is believed that the poor

predominant conformer was due to the strongest microwave absorption band arising from the molecules in the excited state where the NCO moiety is freely rotating. The weaker band at 21000 MHz (Fig. 6) gives a value of ~ 4270 MHz for the B+C value. The weakness of the band is due to the small number of molecules in the bound state. By using the B+C value of 4270 MHz, the *trans* conformer is more consistent as the more stable conformer and not the *skew* form.

In addition to the eighteen transitions reported in Table I, it was possible to assign many of the $K_a = 2$ for $J' = 3$ but they could not be used to obtain the centrifugal distortion constants. This failure of the centrifugal distortion analysis is similar to the problem observed in the study of the microwave spectrum of *cis* cyclopropylisocyanate [43]. For this molecule, the frequencies of the $K_a = 0, 1$, and 2 transitions corresponded within the standard error with the prediction of the spectrum including centrifugal distortion effects. However, the frequencies of the lines with $K_a > 2$ showed considerable deviations from the predicted values and increased significantly with increased K_a value [43] which was observed for the transitions measured for isopropylisocyanate. There has been a detailed analysis of the distortion constants for small molecules which have large amplitude, low frequency vibrations [7] where the authors have shown that the energy maps of such molecules follow closely the predictions from the mathematical concept of non-trivial monodromy. It is expected that the large number of microwave lines (Table I) that were assigned by their quadrupole hyperfine splittings would have similar energy maps. From the splitting observed for the transitions, quadrupole coupling constants were obtained (Table II). Additionally, the quadrupole coupling constants were predicted from the ab initio and density functional theory calculations and these values are also listed in Table II for comparison to the experimentally determined values. Those obtained from the B3LYP/6-311+G(d,p) calculations agree the best with the experimental values but the

31], the “pseudo gas phase” spectrum shows only small frequency shifts compared with the spectrum of the gas. A significant advantage of this type of cryogenic spectroscopic study is that the conformer bands are better resolved in comparison with those in the spectrum of the gas. This is particularly important because most of the conformer bands for this molecule were expected to be observed within a few wavenumbers of each other. The different conformer bands that are expected to be clearly identified are those in the spectral region below 1000 cm^{-1} since they have the lowest probability of having intensity contributions from overtones or combination bands.

The sample was dissolved in liquefied xenon solution and the Raman spectra were recorded at six different temperatures. Of the several fundamental modes exhibiting conformer doublets, the 902 cm^{-1} (*trans*) and 943 cm^{-1} (*gauche*) pair (Fig. 7) was initially chosen for the conformational enthalpy determination due to their relatively even baseline, satisfactory band separations, and relatively strong band intensities. The relative intensities of this conformer pair were measured as a function of temperature and their ratios were determined. Six sets of spectral data were obtained for the pair and by application of the van't Hoff equation, $-\ln K = \Delta H/(RT) - \Delta S/R$, the enthalpy difference was determined from a plot of $-\ln K$ versus $1/T$, where $\Delta H/R$ is the slope of the line and K is substituted with the appropriate intensity ratios, i.e. I_{trans}/I_{gauche} . It was assumed that ΔH , ΔS and the ratio of the molar absorption coefficients $\epsilon_{trans}/\epsilon_{gauche}$ are not a function of temperature in the range studied. The conformational enthalpy difference was determined to be $131 \pm 15\text{ cm}^{-1}$ ($1.57 \pm 0.18\text{ kJ/mol}$) from the xenon solution for this pair. One other pair of fundamentals was also utilized ($755\text{ trans}/943\text{ gauche}$), from which a second ΔH value was obtained. The two individual values are listed in Table VII and the statistical average was obtained by treating the data as a single set which gave a value of $115 \pm 13\text{ cm}^{-1}$ ($1.37 \pm$

that the vibrational data indicated that the isopropylisocyanate has a plane of symmetry. In the current study, the most stable conformer has been identified as the *trans* form by both vibrational and rotational data with a second stable *gauche* form.

One of the problems that were consistently encountered for isocyanate substituted molecules is the low barrier to nearly free internal rotation. The quasi-linearity of the NCO group to the isopropyl group has a pronounced effect on the infrared spectra in the gas phase. Many of the bands are relatively non-descript with large bandwidth that are often resolved into several fundamentals in the spectra of the xenon solution and solid. This effect is clearly observed in several spectral regions i.e. ~ 1350 , ~ 1150 , ~ 900 , ~ 760 cm^{-1} . The ~ 900 cm^{-1} band is a single broad peak but four fundamentals (943, 930, 907, 896 cm^{-1}) are observed in this region in the infrared spectrum of the solid. Similarly, the C-N stretching fundamental (~ 760 cm^{-1}) in the infrared spectrum of the gas is very broad with a pronounced shoulder band at ~ 741 cm^{-1} (*gauche* fundamental). As expected, similar breadths are observed for vibrational modes associated with the NCO group. The NCO in- and out-of-plane bends are predicted at 636 and 574 cm^{-1} , respectively, for the *trans* conformer but the band that is observed spanned from 500 to 700 cm^{-1} with two non-descript peaks at 645 and 611 cm^{-1} . These bands were barely resolved in the infrared spectra of the xenon solution as well as the solid. This is not surprising since the NCO fundamentals are often most affected by the low barrier to nearly free internal rotation. A simplified estimate can be made for barrier to internal rotation of the NCO group from the predicted energy differences (Table V) between the *skew* form and the most stable *trans* form and an average value of 128 cm^{-1} is obtained. This very low barrier can result in a very large number of excited vibrational states populated even at dry ice temperature.

Besides giving rise to a lower barrier to internal rotation, the NCO group seems to be

0.15 kJ/mol).

We also carried out a variable temperature study in xenon solution by utilizing infrared spectra in the lower frequency region. The two lines at 407 and 349 cm^{-1} of the gas are the only well resolved conformer doublet where the relative intensities could be measured as a function of temperature in the xenon. Five sets of spectral data were obtained at temperatures varying from -60 to -100°C (Table VII). From this conformer pair, a ΔH value of $109 \pm 13 \text{ cm}^{-1}$ ($1.30 \pm 0.15 \text{ kJ/mol}$) was determined. Additionally, one other conformer pair from the mid-infrared spectra was obtained for ΔH determination. From this conformer pair, intensity ratio of I_{757}/I_{742g} were collected from 9 different temperatures at 5° interval starting at -60°C , and an enthalpy difference of $121 \pm 9 \text{ cm}^{-1}$ ($1.45 \pm 0.11 \text{ kJ/mol}$) was obtained. Unfortunately, most of the conformer bands were separated by very few wavenumbers so it was not possible to obtain another conformer pair from the infrared spectra.

The four individual ΔH values are listed in Table VII and the statistical average with standard deviation of one sigma was obtained by treating all the data as a single set which gives a value of $115 \pm 7 \text{ cm}^{-1}$ ($1.38 \pm 0.08 \text{ kJ/mol}$). Although the statistical uncertainty is relatively small, it does not take into account possible contribution from combination or overtone bands from the other conformer contributing to the measured fundamental band intensities. The variations of ΔH values are undoubtedly due to these types of interferences. Therefore, a more probable uncertainty is 10% which gives $115 \pm 11 \text{ cm}^{-1}$ ($1.38 \pm 0.13 \text{ kJ/mol}$) for ΔH .

DISCUSSION

From the earlier vibrational study it was suggested [8] that there is only one stable *skew* conformer and that there were little indications of a second conformer. However, it was noted

affecting the barrier to internal rotation of the methyl rotor as well. It has been shown [32-36] that ab initio calculations with a relatively small basis set can be used to obtain the barrier to internal rotation of the CH₃ rotor. For the CH₃ rotor of the isopropyl group in this study, the predicted barriers from the ab initio calculations with the following basis sets are: MP2(full)/6-31G(d), $\Delta E=1584\text{ cm}^{-1}$; MP2/6-311G(d,p), $\Delta E=1545\text{ cm}^{-1}$; and MP2/6-311+G(d,p), $\Delta E=1496\text{ cm}^{-1}$. These values are consistent with the predicted barrier to methyl rotation in ethylisocyanate [18] from the following basis sets: MP2(full)/6-31G(d), $\Delta E=1520\text{ cm}^{-1}$ and MP2/6-311+G(d,p), $\Delta E=1482\text{ cm}^{-1}$. These predicted values are similar to the experimentally determined barrier of $1546.2 \pm 14.2\text{ cm}^{-1}$ for ethylisocyanate [18] obtained by utilizing the fundamental torsional frequency. It is interesting to point out that the NCO group appears to increase the methyl barrier value for the isopropyl group compared to those substituted with H, Cl, Br, and I i.e. (CH₃)₂CH₂ [37] = 1165 cm^{-1} (CH₃)₂CHCl [23] = 1231 cm^{-1} , (CH₃)₂CHBr [38] = 1490 cm^{-1} , (CH₃)₂CHI [38] = 1444 cm^{-1} . A similar trend for the methyl barrier is observed for the ethyl compounds where the NCO (1546 cm^{-1}) of ethylisocyanate is substituted with H [39] = 1028 cm^{-1} , F [40] = 1165 cm^{-1} , Cl [41] = 1287 cm^{-1} and Br [42] = 1287 cm^{-1} .

The low barrier to internal rotation of the NCO group makes the assignment of the microwave spectra quite difficult particularly when the centrifugal distortion constants are expected to have relatively large values. This probably contributed to the previous study [8] of isopropylisocyanate in which it was incorrectly concluded that the *skew* conformer was the most stable form based on the determined B+C value. The B+C value of 4031 MHz fitted more favorably with the calculated B+C value of 4024 MHz for the *skew* form than the calculated values of 3727 MHz for the *gauche* form or 4236 MHz for the *trans* conformer. A possible reason the rotational constants reported previously did not give the correct *trans* conformer as the

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FIGURE CAPTIONS

- Fig. 1 Conformers of isoproylisocyanate: (a) *trans*, (b) *gauche*, (c) *cis*, (d) *skew*
- Fig. 2 Observed and predicted (MP2(full)/6-311+G(d,p)) infrared spectra of isoproylisocyanate: (A) Gas; Simulated spectrum of (B) mixture of *gauche* and *trans* conformers with $\Delta H = 115 \text{ cm}^{-1}$, (C) pure *gauche* conformer, and (D) pure *trans* conformer.
- Fig.3 Observed and predicted (MP2 (full)/6-311+G(d,p)) infrared spectra of isoproylisocyanate: (A) Solid; Simulated spectrum of (B) mixture of *gauche* and *trans* conformers with $\Delta H = 115 \text{ cm}^{-1}$, (C) pure *gauche* conformer, and (D) pure *trans* conformer.
- Fig. 4 Infrared spectra of isoproylisocyanate: (A) Gas; (B) Xenon solution at -100°C .
- Fig. 5 Observed and predicted (MP2(full)/6-311+G(d,p)) Raman spectra of isoproylisocyanate: (A) Xenon solution at -100°C ; Simulated spectrum of (B) mixture of *gauche* and *trans* conformers with $\Delta H = 115 \text{ cm}^{-1}$, (C) pure *gauche* conformer, and (D) pure *trans* conformer.
- Fig. 6 Low resolution microwave spectrum of isoproylisocyanate.
- Fig. 7 Temperature dependence of the 902 cm^{-1} (*trans*) and the 943 cm^{-1} (*gauche*) Raman bands of isoproylisocyanate dissolved in liquid xenon.
- Fig. 8 Potential energy curve of isoproylisocyanate as a function of the dihedral angle $\text{C}=\text{N}-\text{C}_\alpha-\text{H}_3$ obtained from MP2(full)/6-311G(2d,2p) calculations (dashed line) and MP2(full)/aug-cc-PVDZ calculations (solid line).

1a) Trans

1b) Gauche

1c) Cis

1d) Skew

Table I. Rotational transitional frequencies (MHz) for *trans* isopropylisocyanate in the ground vibrational state.

Transition	F' $\leftarrow$ F	ν (obs)	$\Delta\nu$ (obs-calc)
$3_{0,3} \leftarrow 2_{0,2}$	$2 \leftarrow 1$	12609.961	0.210
	$2 \leftarrow 2$	12608.683	0.207
	$3 \leftarrow 2$	12609.822	0.212
	$3 \leftarrow 3$	12610.643	0.213
	$4 \leftarrow 3$	12609.800	0.210
$2_{1,1} \leftarrow 1_{0,1}$	$1 \leftarrow 0$	13483.498	0.047
	$1 \leftarrow 1$	13481.564	0.039
	$2 \leftarrow 1$	13482.321	0.041
	$2 \leftarrow 2$	13483.094	0.044
	$3 \leftarrow 2$	13482.608	0.043
$4_{0,4} \leftarrow 3_{0,3}$	$3 \leftarrow 2$	16744.483	-0.150
	$3 \leftarrow 3$	16743.348	-0.150
	$4 \leftarrow 3$	16744.416	-0.147
	$4 \leftarrow 4$	16745.258	-0.145
	$5 \leftarrow 4$	16744.406	-0.150
$3_{1,2} \leftarrow 2_{0,2}$	$2 \leftarrow 1$	18165.799	-0.075
	$3 \leftarrow 2$	18165.499	-0.066
	$4 \leftarrow 3$	18165.606	-0.064

Table II. Rotational (MHz), centrifugal distortion (kHz) and quadrupole coupling (MHz) constants for the *trans* and *gauche* conformers of isopropylisocyanate.

	<i>trans</i>				<i>gauche</i>		
	MP2/6- 31G(d)	MP2/6- 311+G(d,p)	B3LYP /6- 311+G(d,p)	MW	MP2/6- 31G(d)	MP2/6- 311+G(d,p)	B3LYP /6- 311+G(d,p)
<i>A</i>	6693	6596	6727	6693.235(149)	8221	8216	8122
<i>B</i>	2226	2271	2197	2263.103(34)	2008	2054	2011
<i>C</i>	1939	1983	1904	1960.050(24)	1695	1728	1692
Δ_J	0.874	0.937	0.974		0.671	0.607	0.932
Δ_{JK}	37.97	27.68	87.09		33.70	12.60	12.16
Δ_K	-30.33	-20.68	-77.65		-27.24	-4.24	-4.52
δ_J	0.0197	0.0188	0.0144		0.1035	0.081	0.134
δ_K	12.45	8.81	15.65		16.835	6.796	4.929
χ_{aa}	2.6679	2.8161	2.8863	2.487(38)	2.8253	2.8809	2.9105
χ_{bb}	-1.8676	-1.9331	-1.6959	-1.343(59)	-1.3091	-1.2713	-1.4687
χ_{cc}	-0.8003	-0.8830	-1.1904	-1.144(46)	-1.5162	-1.6096	-1.4418

Table III. Calculated (MP2(full)/6-31G(d)) and observed vibrational frequencies (cm^{-1}) of isopropylisocyanate for the *trans* conformer.

Vib. No	Approx. description	MP2 scaled ^a	MP2	IR int ^b	Raman ac ^c	Infrared				Raman			PED ^d	A	C
						Gas	Xe	Solid	Gas	Xe	Solid				
A' ν_1	CH ₃ antisym. stretch	3213	3014	16.0	75.9	2990	3017	2291	2291	~2979	2989	70S ₁ , 30S ₂	23	77	
A'' ν_{20}	CH ₃ antisym. stretch	3212	3013	11.6	42.9	2990	3017	2291	—	2982	—	69S ₂₀ , 31S ₂₁			
A' ν_2	CH ₃ antisym. stretch	3202	3004	42.8	91.3	2979	2976	2982	~2975	~2979	2982	70S ₂ , 28S ₁	79	21	
A'' ν_{21}	CH ₃ antisym. stretch	3196	2998	0.3	6.0	—	—	—	—	—	—	69S ₂₁ , 31S ₂₀			
A' ν_3	CH stretch	3133	2939	15.1	91.2	2935	2932	2942	2939	2943	2940	95S ₃	32	67	
A' ν_4	CH ₃ symmetric stretch	3108	2915	8.7	195.6	2924	—	2929	2925	2922	2924	98S ₄	48	52	
A'' ν_{22}	CH ₃ symmetric stretch	3106	2913	9.9	2.0	—	2908	—	—	2909	—	99S ₂₂			
A' ν_5	NCO antisym. stretch	2386	2263	808.8	1.0	~2272	2265	2265	2270	2262	2261	98S ₅	91	9	
A' ν_6	CH ₃ antisym. def.	1570	1473	4.8	2.2	1476	1470	1474	1477	1470	1472	84S ₆	59	41	
A' ν_7	CH ₃ antisym. def.	1559	1462	9.0	23.5	1462	1456	1462	1462	1456	1454	87S ₇	21	79	
A'' ν_{23}	CH ₃ antisym. def.	1549	1453	0.0	25.5	—	—	—	—	~1447	1449	88S ₂₃			
A'' ν_{24}	CH ₃ antisym. def.	1548	1452	2.3	4.3	—	—	1447	—	—	—	85S ₂₄			
A' ν_8	NCO sym. stretch	1479	1404	4.0	6.3	1424	1425	1431	1433	1426	1430	31S ₈ , 46S ₉	57	43	
A' ν_9	CH ₃ symmetric def.	1471	1396	17.0	14.3	1392	1387	1387	1389	1387	1387	50S ₉ , 30S ₈	50	50	
A'' ν_{25}	CH ₃ symmetric def.	1457	1383	12.4	2.4	1375	1370	1372	—	1372	1368	90S ₂₅			
A' ν_{10}	CH in-plane bend	1415	1345	37.2	15.7	~1332	1335	1337	1335	~1329	1328	53S ₁₀ , 20S ₁₆	93	7	
A'' ν_{26}	CH out-of-plane bend	1412	1341	2.5	6.9	~1332	—	—	—	~1329	—	50S ₂₆ , 24S ₃₁ , 10S ₂₉			
A' ν_{11}	CH ₃ rock	1236	1179	3.8	1.4	1167	1165	1168	1166	1164	1168	63S ₁₁ , 12S ₁₇ , 10S ₁₃	0	100	
A'' ν_{27}	CC ₂ antisym. stretch	1198	1143	6.7	3.3	1134	1133	1134	—	1133	1135	50S ₂₇ , 27S ₂₈ , 18S ₃₁			
A' ν_{12}	CH ₃ rock	1157	1104	45.0	9.3	1103	1103	1102	1106	1101	1101	59S ₁₂ , 17S ₁₀ , 10S ₈	98	2	

Table III Continued.

Vib. No	Approx. description	MP2	MP2 scaled ^a	IR int ^b	Raman act ^c	Infrared			Raman			PED ^d	A	C
						Gas	Xe	Solid	Gas	Xe	Solid			
A'' v ₂₈	CH ₃ rock	990	939	0.0	4.2	—	—	—	—	—	—	60S ₂₈ , 29S ₂₇		
A'' v ₂₉	CH ₃ rock	968	919	1.1	0.6	—	925	930	—	925	931	81S ₂₉		
A' v ₁₃	CC ₂ symmetric stretch	944	894	6.5	7.9	901	903	896	—	902	896	56S ₁₃ , 17S ₁₄ , 13S ₁₁	77	23
A' v ₁₄	C–N stretch	788	749	15.3	11.3	~760	757	~745	767	755	—	45S ₁₄ , 23S ₁₃ , 15S ₈	52	48
A' v ₁₅	NCO in-plane bend	636	633	24.6	0.8	645	638	~621	648	639	623	70S ₁₅ , 12S ₁₉ , 10S ₁₆	39	61
A'' v ₃₀	NCO out-of-plane bend	574	574	20.8	0.3	587	~580	575	—	582	578	96S ₃₀		
A' v ₁₆	CC ₂ wag	493	478	3.9	0.9	478	475	477	—	~469	476	47S ₁₆ , 13S ₁₅	69	31
A'' v ₃₁	CC ₂ twist	422	419	4.7	0.3	408	408	411	—	407	413	53S ₃₁ , 36S ₂₆		
A' v ₁₇	CC ₂ deformation	366	363	0.4	0.2	355		363		—	350	77S ₁₇	32	68
A' v ₁₈	CH ₃ torsion	301	286	0.4	0.0	276		—	—	271		97S ₁₈	81	19
A'' v ₃₂	CH ₃ torsion	268	254	0.0	0.0							99S ₃₂		
A' v ₁₉	CNC bend	122	122	4.9	2.3	125		140		126		89S ₁₉	90	10
A'' v ₃₃	C–N torsion	45	45	0.4	2.9	53		—	—	56		100S ₃₃		

Table IV. Calculated (MP2(full)/6-31G(d)) and observed vibrational frequencies (cm^{-1}) of isopropylisocyanate for the *gauche* conformer.

Vib. No	Approx. description	MP2	MP2 scaled ^a	IR int ^b	Raman act ^c	Infrared			Raman Xenon (-100°C)	PED ^d	A	B	C
						Gas	Xenon	Solid					
ν_1	CH ₃ antisym. stretch	3215	3016	16.2	58.3					56S ₁ , 34S ₃	9	43	48
ν_2	CH ₃ antisym. stretch	3210	3011	28.7	79.6					48S ₂ , 31S ₁ , 19S ₃	14	14	72
ν_3	CH ₃ antisym. stretch	3206	3007	12.3	40.9					46S ₃ , 30S ₂ , 18S ₄	98	0	2
ν_4	CH ₃ antisym. stretch	3201	3003	9.7	33.9					75S ₄ , 18S ₂	90	10	0
ν_5	CH ₃ symmetric stretch	3113	2921	10.4	127.8			2925		71S ₅ , 29S ₆	78	9	13
ν_6	CH ₃ symmetric stretch	3108	2915	10.5	54.6					71S ₆ , 29S ₅	1	98	1
ν_7	CH stretch	3103	2911	20.9	97.4					98S ₇	14	0	86
ν_8	NCO antisym. stretch	2392	2270	849.5	1.0					98S ₈	99	1	0
ν_9	CH ₃ antisym. def.	1572	1475	6.2	3.3					84S ₉	3	6	91
ν_{10}	CH ₃ antisym. def.	1559	1462	6.0	27.4					87S ₁₀	1	0	99
ν_{11}	CH ₃ antisym. def.	1549	1453	0.4	19.0					94S ₁₁	56	41	3
ν_{12}	CH ₃ antisym. def.	1547	1451	2.0	10.2					91S ₁₂	10	90	0
ν_{13}	CH ₃ symmetric def.	1478	1403	23.3	3.1	~1424	~1425	1419	~1426	88S ₁₃	92	1	6
ν_{14}	CH ₃ symmetric def.	1469	1393	34.3	24.2					51S ₁₄ , 20S ₂₄ , 13S ₁₅	92	0	8
ν_{15}	CH out-of-plane bend	1458	1383	15.6	10.2	1357	1352	1355	1350	74S ₁₅ , 13S ₁₄	2	97	1
ν_{16}	CH in-plane bend	1410	1340	15.8	5.0	~1332		1344		43S ₁₆ , 20S ₂₈	84	16	0
ν_{17}	NCO symmetric stretch	1397	1326	50.2	8.1	~1332	1328	1325		57S ₁₇ , 19S ₂₇	98	2	0
ν_{18}	CH ₃ rock	1236	1180	13.4	1.9					61S ₁₈ , 13S ₂₉ , 11S ₂₃	92	2	6
ν_{19}	CC ₂ antisym. stretch	1201	1145	11.7	4.7	1128	~1133	1130		47S ₁₉ , 26S ₂₁ , 20S ₂₈	47	53	0
ν_{20}	CH ₃ rock	1167	1113	10.7	4.3	~1112	1116	1119	1122	55S ₂₀ , 22S ₁₇	56	9	35

Table IV continued

Vib. No	Approx. description	MP2	MP2 scaled ^a	IR int ^b	Raman act ^c	Infrared			Raman Xenon (-100°C)	PED ^d	A B C		
						Gas	Xenon	Solid					
ν_{21}	CH ₃ rock	995	944	0.3	3.6		944	943	943	58S ₂₁ , 30S ₁₉	0	88	12
ν_{22}	CH ₃ rock	967	917	1.3	0.5				928	81S ₂₂	8	91	1
ν_{23}	CC ₂ symmetric stretch	955	905	7.9	6.7	~905	903	907		54S ₂₃ , 14S ₂₄ , 12S ₁₈	70	15	15
ν_{24}	CN stretch	784	747	10.1	13.2	~741	742	~745	742	41S ₂₄ , 20S ₂₃ , 12S ₁₄ , 10S ₂₅	5	70	25
ν_{25}	NCO in-plane bend	621	619	21.0	0.9	~611		~621		79S ₂₅	54	35	11
ν_{26}	NCO out-of-plane bend	571	571	19.6	0.4	580	580	575		98S ₂₆	1	35	64
ν_{27}	CC ₂ wag	471	456	4.9	0.8	456	456	456	~460	50S ₂₇ , 13S ₂₉ , 10S ₁₇	69	17	15
ν_{28}	CC ₂ twist	423	420	14.6	1.1	~415		417		42S ₂₈ , 27S ₁₆	84	15	1
ν_{29}	CC ₂ def.	354	351	2.3	0.7		349		351	61S ₂₉ , 14S ₂₇	99	1	0
ν_{30}	CH ₃ torsion	294	279	0.5	0.1					94S ₃₀	81	5	14
ν_{31}	CH ₃ torsion	256	242	0.0	0.0					96S ₃₁	89	9	2
ν_{32}	CNC bend	120	120	4.8	2.2					89S ₃₂	99	0	1
ν_{33}	CN torsion	34	34	0.7	2.9					100S ₃₃	7	22	71

^a Force constant scaling factors: 0.88 for CH stretches; 0.9 for all other modes.^b Infrared intensities in km/mol.^c Raman activities in Å⁴/u.^d PEDs from MP2 scaled calculation

Table V. Calculated electronic energies (hartree) and energy differences^a (cm⁻¹) for the *trans*, *gauche*, *skew* and *cis* conformers of isopropylisocyanate

Method / Basis set	Basis Functions	<i>Trans</i>	<i>Gauche</i>	<i>Skew</i>	<i>Cis</i>
MP2(full)/6-31G(d)	104	-285.747424	131	162	186
MP2(full)/cc-PVDZ	119	-285.801139	120	177	147
MP2(full)/6-31+G(d)	128	-285.763357	60	139	152
MP2(full)/TZVP	156	-286.012456	124	162	183
MP2(full)/6-311G(d,p)	150	-286.001377	111	190	132
MP2(full)/6-311+G(d,p)	174	-286.010755	85	164	184
MP2(full)/aug-cc-PVDZ	201	-285.858003	80	127	180
MP2(full)/6-311G(2d,2p)	201	-286.079008	88	98	129
MP2(full)/6-311+G(2d,2p)	225	-286.087200	61	71	124
MP2(full)/cc-PVTZ	278	-286.161888	137	127	227
MP2(full)/6-311G(2df,2pd)	278	-286.183627	113	109	157
MP2(full)/6-311+G(2df,2pd)	302	-286.190707	79	79	153
MP2(full)/6-311G(3df,3pd)	329	-286.207187	70	83	122
MP2(full)/6-311+G(3df,3pd)	353	-286.213089	110	108	182
MP2(full)/aug-cc-PVTZ	437	-286.201499	51	–	195
MP2(full)/cc-PVQZ	540	-286.336201	87	–	168
<hr/>					
B3LYP/6-31G(d)	104	-286.622796	71	82	103
B3LYP/6-31+G(d)	128	-286.634178	20	51	45
B3LYP/6-311G(d,p)	150	-286.705382	16	69	20
B3LYP/6-311+G(d,p)	174	-286.710621	13	55	35
B3LYP/6-311G(2d,2p)	201	-286.714378	12	48	7
B3LYP/6-311+G(2d,2p)	225	-286.719732	18	36	30
B3LYP/6-311G(2df,2pd)	278	-286.724158	24	51	20
B3LYP/6-311+G(2df,2pd)	302	-286.72909	19	35	38
B3LYP/6-311G(3df,3pd)	329	-286.727557	-11	32	6
B3LYP/6-311+G(3df,3pd)	353	-286.731983	24	51	54

^a Energy difference are relative to the *trans* conformer.

Table VI. Structural parameters (Å and degree), rotational constants (MHz) and dipole moment (debye) for *trans* isopropylisocyanate from the 6-311+G(d,p) basis set and adjusted r_0 parameters.

Structural Parameters	<i>Trans</i>		<i>Gauche</i>		Adj. r_0		estimated	
	MP2	B3LYP	MP2	B3LYP	MW ^{a,b}	E.D.	<i>Trans</i>	<i>Gauche</i>
r C ₄ -N	1.457	1.460	1.458	1.462	1.471	1.460(8)	1.453(3)	1.454(3)
r N=C	1.217	1.201	1.216	1.200	1.171	1.214(6)	1.208(5)	1.207(5)
r C=O	1.181	1.175	1.180	1.174	1.207	1.184(4)	1.165(3)	1.164(3)
r C ₄ -C _{6,7}	1.524	1.531	1.521/1.524	1.528/1.531	1.522	1.534(5)	1.524(3)	1.521/1.524(3)
r C ₄ -H ₅	1.094	1.093	1.096	1.096	1.091	1.090*	1.094(2)	1.096(2)
r C _{6,7} -H _{10,13}	1.095	1.094	1.093/1.094	1.096/1.093	1.091	1.114(5)	1.095(2)	1.093/1.094(2)
r C _{6,7} -H _{8,11}	1.094	1.093	1.094/1.094	1.093/1.093	1.091	1.114(5)	1.094(2)	1.094/1.094(2)
r C _{6,7} -H _{9,12}	1.092	1.092	1.092/1.093	1.092/1.093	1.091	1.114(5)	1.092(2)	1.092/1.093(2)
∠ N=C=O	172.6	173.7	172.8	173.9		159.0(30)	172.6(5)	172.8(5)
∠ C ₄ N=C	133.2	138.9	134.5	139.3	139.0	132.6(10)	137.0(5)	138.32(5)
∠ NC ₄ C _{6,7}	110.3	110.7	108.3/110.5	108.8/110.7		110.0(5)	109.4(5)	107.4/109.6(5)
∠ C ₆ C ₄ C ₇	112.2	112.6	112.0	112.3	112.7	114.7(9)	113.1(5)	113.0(5)
∠ NC ₄ H ₅	105.7	105.5	107.6	107.3		105.0*	105.7(5)	107.6(5)
∠ C _{6,7} C ₄ H ₅	109.1	108.5	109.0/109.2	108.6/108.9	109.9		109.4(5)	109.3/109.6(5)
∠ C ₄ C _{6,7} H _{8,11}	110.1	110.1	110.0/110.1	110.2/110.1	109.9	107*	110.1(5)	110.0/110.1(5)
∠ C ₄ C _{6,7} H _{9,12}	110.7	110.9	110.6/111.0	110.8/111.2	109.9	107*	110.7(5)	110.6/111.0(5)
∠ C ₄ C _{6,7} H _{10,13}	110.1	110.7	110.0/109.9	110.5/110.5	109.9	107*	110.1(5)	110.0/109.9(5)
τ C=N ₂ C ₄ H ₅	180.0	180.0	71.3	58.5			180.0	71.3
A	6596	6727	8216	8128	6693.235		6693.17	8133
B	2271	2197	2054	2002	2263.103		2263.99	2061
C	1983	1904	1728	1685	1960.050		1960.15	1732
μ _a	3.430	3.345	3.218	3.151			3.427	3.206
μ _b	-	-	0.862	0.596			-	0.833
μ _c	0.297	0.125	0.679	0.655			0.270	0.671
μ _t	3.4428	3.347	3.400	3.273			3.438	3.380

^a Ref.[8] assumed structural parameters, rotational study from current study.

* fixed ^b Rotational constants listed were obtained from this study.

Table VII. Temperature and intensity ratios of the conformer bands of isopropylisocyanate from Raman and infrared spectra of the liquid xenon solution.

	T(°C)	1/T ($\times 10^{-3}$ K $^{-1}$)	Raman		Infrared	
			I _{755t} / I _{943g}	I _{902t} / I _{943g}	I _{408t} / I _{349g}	I _{757t} / I _{742g}
Liquid xenon	-50.0	4.4813	2.1905	10.0556		
	-60.0	4.6915	2.3294	10.6739	9.6034	10.4091
	-65.0	4.8042				10.7727
	-70.0	4.9225	2.4651	11.3191	9.8189	11.0000
	-75.0	5.0467				10.9130
	-80.0	5.1773	2.5000	12.0521	10.1679	11.1207
	-85.0	5.3149				11.7467
	-90.0	5.4600	2.6614	12.4490	10.5109	12.0870
	-95.0	5.6132				12.2979
	-100.0	5.7753	2.6196	12.8000	11.4429	12.5532
ΔH^a			98 $\pm$ 19	131 $\pm$ 15	109 $\pm$ 13	121 $\pm$ 9
			115 $\pm$ 13 cm $^{-1}$ (1.37 $\pm$ 0.15 kJ/mol)		116 $\pm$ 7 cm $^{-1}$ (1.39 $\pm$ 0.09 kJ/mol)	

^a Average value obtained by utilizing all data as a single set gives $\Delta H = 115 \pm 7$ cm $^{-1}$ (1.38 $\pm$ 0.08 kJ/mol) with the *trans* conformer more stable.

Table IS. Transitions not utilized for the determination of the rotational constants for isopropylisocyanate.

Transition	F' $\leftarrow$ F	$\nu(\text{obs})$	Transition	F' $\leftarrow$ F	$\nu(\text{obs})$
$3_{1,3} \leftarrow 2_{1,2}$	$2 \leftarrow 1$	12203.637	$2_{1,1} \leftarrow 1_{0,1}$	$1 \leftarrow 0$	13483.498
	$4 \leftarrow 3$	12203.861	$5_{0,5} \leftarrow 4_{1,3}$	$5 \leftarrow 4$	14546.221
	$3 \leftarrow 2$	12203.966		$6 \leftarrow 5$	14546.259
	$3 \leftarrow 3$	12204.206	$4_{1,4} \leftarrow 3_{1,3}$	$5 \leftarrow 4$	16255.003
$3_{0,3} \leftarrow 2_{0,2}$	$2 \leftarrow 2$	12608.683		$3 \leftarrow 2$	16255.032
	$4 \leftarrow 3$	12609.800		$4 \leftarrow 3$	16255.099
	$3 \leftarrow 2$	12609.822	$4_{0,4} \leftarrow 3_{0,3}$	$3 \leftarrow 3$	16743.348
	$2 \leftarrow 1$	12609.961		$5 \leftarrow 4$	16744.406
$3_{2,2} \leftarrow 2_{2,1}$	$3 \leftarrow 3$	12610.643		$4 \leftarrow 3$	16744.416
	$2 \leftarrow 1$	12663.800		$3 \leftarrow 2$	16744.483
	$4 \leftarrow 3$	12664.261		$4 \leftarrow 4$	16745.258
	$3 \leftarrow 2$	12665.090	$4_{2,3} \leftarrow 3_{2,2}$	$3 \leftarrow 2$	16874.065
$3_{2,1} \leftarrow 2_{2,0}$	$2 \leftarrow 1$	12723.833		$5 \leftarrow 4$	16874.160
	$4 \leftarrow 3$	12724.294		$4 \leftarrow 3$	16874.510
	$3 \leftarrow 2$	12725.134	$4_{3,2} \leftarrow 3_{3,1}$	$3 \leftarrow 2$	16904.906
	$3 \leftarrow 3$	12831.783		$5 \leftarrow 4$	16905.204
$3_{2,2} \leftarrow 3_{1,2}$	$4 \leftarrow 4$	12831.807		$4 \leftarrow 3$	16905.975
	$2 \leftarrow 2$	12831.939	$4_{3,1} \leftarrow 3_{3,0}$	$3 \leftarrow 2$	16907.699
	$4 \leftarrow 3$	13114.505		$5 \leftarrow 4$	16907.997
	$2 \leftarrow 1$	13114.526		$4 \leftarrow 3$	16908.766
$3_{1,2} \leftarrow 2_{1,1}$	$3 \leftarrow 2$	13114.731	$4_{2,2} \leftarrow 3_{2,1}$	$3 \leftarrow 2$	17022.634
	$1 \leftarrow 1$	13481.564		$5 \leftarrow 4$	17022.731
	$2 \leftarrow 1$	13482.321		$4 \leftarrow 3$	17023.092
	$3 \leftarrow 2$	13482.608	$4_{1,3} \leftarrow 3_{1,2}$	$3 \leftarrow 3$	17466.389
$2_{1,1} \leftarrow 1_{0,1}$	$2 \leftarrow 2$	13483.094		$5 \leftarrow 4$	17467.316

Table IS. Continued

Transition	$F' \leftarrow F$	$\nu(\text{obs})$
$4_{1,3} \leftarrow 3_{1,2}$	$3 \leftarrow 2$	17467.359
	$4 \leftarrow 3$	17467.418
	$4 \leftarrow 4$	17468.131
$3_{1,2} \leftarrow 2_{0,2}$	$3 \leftarrow 2$	18165.499
	$4 \leftarrow 3$	18165.606
	$2 \leftarrow 1$	18165.799
$5_{1,5} \leftarrow 4_{1,4}$	$4 \leftarrow 4$	20292.643
	$6 \leftarrow 5$	20293.454
	$4 \leftarrow 3$	20293.480
	$5 \leftarrow 4$	20293.509
	$5 \leftarrow 5$	20294.172
$5_{0,5} \leftarrow 4_{0,4}$	$4 \leftarrow 4$	20823.910
	$5 \leftarrow 4$	20824.935
	$6 \leftarrow 5$	20824.935
	$4 \leftarrow 3$	20824.986
	$5 \leftarrow 5$	20825.786
$5_{2,4} \leftarrow 4_{2,3}$	$4 \leftarrow 3$	21073.983
	$6 \leftarrow 5$	21074.007
	$5 \leftarrow 4$	21074.183
$5_{2,3} \leftarrow 4_{2,2}$	$4 \leftarrow 3$	21365.971
	$6 \leftarrow 5$	21365.994
	$5 \leftarrow 4$	21366.188
$5_{1,4} \leftarrow 4_{1,3}$	$6 \leftarrow 5$	21802.574
	$4 \leftarrow 3$	21802.607
	$5 \leftarrow 4$	21802.630

Table 2S. Symmetry coordinates for trans form of isopropylisocyanate.

Approximate description		Symmetry coordinate definitions ^a
A'	CH ₃ antisymmetric stretch	$S_1 = r_2 - r_6 + r_3 - r_7$
	CH ₃ antisymmetric stretch	$S_2 = 2r_4 - r_2 - r_6 + 2r_5 - r_3 - r_7$
	CH stretch	$S_3 = r_1$
	CH ₃ symmetric stretch	$S_4 = r_4 + r_2 + r_6 + r_5 + r_3 + r_7$
	NCO antisymmetric stretch	$S_5 = R_2 - R_3$
	CH ₃ antisymmetric deformation	$S_6 = 2\alpha_1 - \alpha_3 - \alpha_5 + 2\alpha_2 - \alpha_4 - \alpha_6$
	CH ₃ antisymmetric deformation	$S_7 = \alpha_3 - \alpha_5 + \alpha_4 - \alpha_6$
	CH ₃ symmetric deformation	$S_8 = \alpha_1 + \alpha_3 + \alpha_5 - \beta_7 - \beta_3 - \beta_5 + \alpha_2 + \alpha_4 + \alpha_6 - \beta_8 - \beta_4 - \beta_6$
	CH in-plane bend	$S_9 = \gamma$
	CH ₃ rock	$S_{10} = \beta_3 - \beta_5 + \beta_4 - \beta_6$
	CH ₃ rock	$S_{11} = 2\beta_7 - \beta_3 - \beta_5 + 2\beta_8 - \beta_4 - \beta_6$
	C–N stretch	$S_{12} = R_1$
	CC ₂ symmetric stretch	$S_{13} = R_4 + R_5$
	NCO symmetric stretch	$S_{14} = R_2 + R_3$
	NCO in-plane bend	$S_{15} = \pi$
	CC ₂ wag	$S_{16} = \eta_1 + \eta_2$
	CC ₂ deformation	$S_{17} = 4\phi - \eta_1 - \eta_2 - \beta_1 - \beta_2$
	CH ₃ torsion	$S_{18} = \tau_2 - \tau_3$
	CNC bend	$S_{19} = \sigma$
A''	CH ₃ antisymmetric stretch	$S_{20} = r_2 - r_6 - r_3 + r_7$
	CH ₃ antisymmetric stretch	$S_{21} = 2r_4 - r_2 - r_6 - 2r_5 + r_3 + r_7$
	CH ₃ symmetric stretch	$S_{22} = r_4 + r_2 + r_6 - r_5 - r_3 - r_7$
	CH ₃ antisymmetric deformation	$S_{23} = 2\alpha_1 - \alpha_3 - \alpha_5 - 2\alpha_2 + \alpha_4 + \alpha_6$
	CH ₃ antisymmetric deformation	$S_{24} = \alpha_3 - \alpha_5 - \alpha_4 + \alpha_6$
	CH ₃ symmetric deformation	$S_{25} = \alpha_1 + \alpha_3 + \alpha_5 - \beta_7 - \beta_3 - \beta_5 - \alpha_2 - \alpha_4 - \alpha_6 + \beta_8 + \beta_4 + \beta_6$
	CH out-of-plane bend	$S_{26} = \eta_1 - \eta_2 + \beta_1 - \beta_2$
	CC ₂ antisymmetric stretch	$S_{27} = R_4 - R_5$
	CH ₃ rock	$S_{28} = 2\beta_7 - \beta_3 - \beta_5 - 2\beta_8 + \beta_4 + \beta_6$
	CH ₃ rock	$S_{29} = \beta_3 - \beta_5 - \beta_4 + \beta_6$
	NCO out-of-plane bend	$S_{30} = \tau_4$
	CC ₂ twist	$S_{31} = \eta_1 - \eta_2 - \beta_1 + \beta_2$
	CH ₃ torsion	$S_{32} = \tau_2 + \tau_3$
	C–N torsion	$S_{33} = \tau_1$

^aNot normalized.