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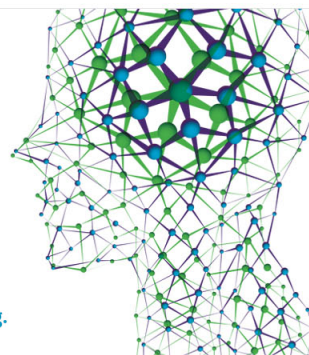
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The effects of nitrogen inversion tunneling, methyl internal rotation, and ^{14}N quadrupole coupling observed in the rotational spectrum of diethyl amine

Ha Vinh Lam Nguyen^{a)} and Wolfgang Stahl*Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany*

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The rotational spectrum of diethyl amine as observed by molecular beam Fourier transform microwave spectroscopy shows splittings due to nitrogen inversion, ^{14}N quadrupole coupling, and internal rotation of the methyl groups. The rotational constants of diethyl amine were determined to be $A = 17.61499170(11)$ GHz, $B = 2.103650248(49)$ GHz, and $C = 1.981332501(47)$ GHz. From the separation between the lowest symmetric and antisymmetric inversion energy level of $E = 760.77062(20)$ MHz a barrier to inversion, using a standard analytical model potential, of 1531 cm^{-1} (18.31 kJ/mol) was deduced. The ^{14}N quadrupole coupling constants were found to be $\chi_{aa} = 2.67576(37)$ MHz, $\chi_{bb} - \chi_{cc} = 4.34144(65)$ MHz, and $|\chi_{bc}| = 2.9199(92)$ MHz. The internal rotation of two equivalent methyl groups gave rise to very narrow multiplets; the torsional barrier was determined to be $1051.74(57)\text{ cm}^{-1}$. The experimental results were supplemented by quantum chemical calculations. © 2011 American Institute of Physics. [doi:10.1063/1.3607992]

I. INTRODUCTION

Many studies on ammonia¹ and small aliphatic amines, such as methyl amine,² ethyl amine,³ dimethyl amine,⁴ trimethyl amine,⁵ and methyl ethyl amine⁶ have been carried out in the microwave region. Most of these compounds, especially primary and secondary amines, show large amplitude motions, e.g., internal rotation of the asymmetric NH_2 rotor and proton inversion tunneling at the nitrogen atom. From investigations on dimethyl amine⁴ and methyl ethyl amine⁶, where due to the inversion tunneling of the proton splittings between the rotational lines of 2646.0 MHz and 1981.0 MHz, respectively, were observed, we expected also in the case of diethyl amine, $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$, splittings on the same order of magnitude.

Moreover, due to the nuclear spin of $I = 1$ of the ^{14}N nucleus and due to its electric quadrupole moment, hyperfine splittings arise and have been reported for several amines. These splittings are usually on the order of 0.5 MHz. Since the experimental resolution of our spectrometer is about 2 kHz,⁷ we expected to be able to resolve the ^{14}N quadrupole hyperfine splittings also in the case of diethyl amine.

In our studies on diethyl ketone, $\text{CH}_3\text{CH}_2(\text{C}=\text{O})\text{CH}_2\text{CH}_3$, a molecule with a very similar structure, we found a barrier to internal rotation of the methyl groups of $771.93(27)\text{ cm}^{-1}$.⁸ Therefore, we expected that in diethyl amine the splittings due to internal rotation of the two equivalent methyl groups could also be resolved and would increase the complexity of the spectra. However, there was another reason to study this molecule. We were interested to find out, whether the torsional barrier of the methyl groups is significantly different if compared to diethyl ketone.

II. EXPERIMENTAL AND QUANTUMCHEMICAL METHODS

A. Microwave spectroscopy

Diethyl amine was purchased from Merck Schuchardt OHG, Hohenbrunn, Germany and used without further purification. Due to its low boiling point of only 328.7 K, mixtures of 1% of diethyl amine in helium at a total pressure of 100 kPa could be easily prepared and served as a sample throughout all measurements. Details of the molecular beam Fourier transform microwave (MB-FTMW) spectrometer are given in Ref. 9 and will not be repeated here. At the beginning of our studies a broadband scan in the range from 14.5 to 16.5 GHz was recorded. All lines observed were re-measured under high resolution conditions. Each frequency is split into two Doppler components. The width of each single component was strongly dependent on the respective transition, however, they were always clearly broader than 1–3 kHz which can be achieved with a molecule such as carbonyl sulfide under comparable conditions.⁷ This might be attributed to partly unresolved internal rotation splittings and hydrogen spin-rotation and spin-spin coupling effects. A sample spectrum will be presented in Sec. III.

B. Quantum chemistry

At the beginning of the experimental work quantum chemical calculations were carried out in order to obtain initial molecular parameters of diethyl amine for spectral assignment purposes. A fully optimized structure was calculated at the MP2/6-311++G(*d,p*) level of theory using the GAUSSIAN 03 program package.¹⁰ The nuclear coordinates referred to principal axes of inertia are available as supplementary material¹¹ (Table S-I), the molecular structure is visualized in Fig. 1. It should be pointed out that all heavy atoms are almost located within one plane. A harmonic frequency

^{a)} Author to whom correspondence should be addressed. Electronic mail: nguyen@pc.rwth-aachen.de.

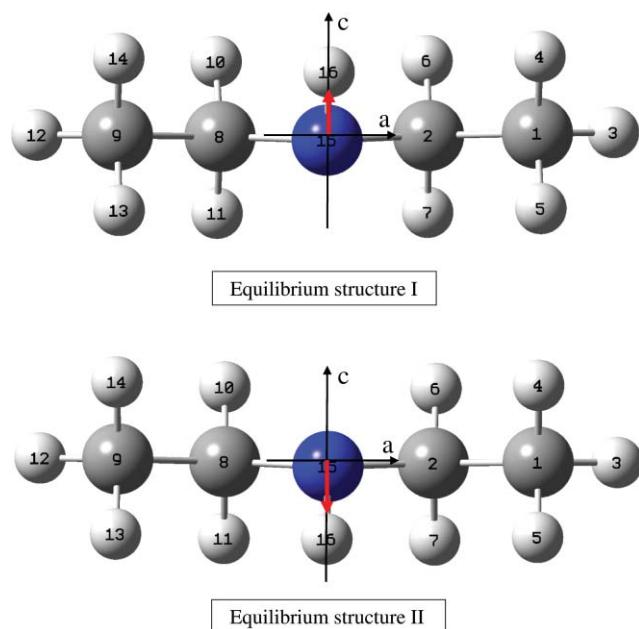


FIG. 1. The two versions of the equilibrium geometry of diethyl amine are obtained by quantum chemical calculation corresponding to the two energy minima of the nitrogen tunneling process. The principal a and c axes of inertia are indicated showing that the dipole component (red arrow) in c direction changes sign upon proton tunneling.

calculation gives all roots real to confirm the equilibrium geometry. The rotational constants of $A = 17.7066$ GHz, $B = 2.1051$ GHz, $C = 1.9831$ GHz indicate that diethyl amine is a near prolate top with an asymmetry parameter of $\kappa = -0.9845$.¹² The molecular dipole moment was found to be $\mu = 1.089$ D with the components $\mu_a = 0.000$ D, $\mu_b = 0.502$ D, and $\mu_c = 0.967$ D referred to the principal axes of inertia. The a component is zero due to a bc mirror plane which is perpendicular to the a axis and which contains the nitrogen atom. Additionally, the electric field gradient tensor at the ^{14}N nucleus was calculated at the MP2/6-311++G(d,p) level of theory. Referred to principal axes of inertia its elements are $q_{aa} = -0.6064$ a.u., $q_{bb} = -0.2250$ a.u., $q_{cc} = 0.8314$ a.u., $q_{bc} = 0.7114$ a.u., and $q_{ab} = q_{ac} = 0$. Using an effective ^{14}N quadrupole moment of 19.41 mb¹³ the quadrupole coupling constants were calculated to be $\chi_{aa} = 2.766$ MHz, $\chi_{bb} = 1.026$ MHz, $\chi_{cc} = -3.792$ MHz, $|\chi_{bc}| = 3.244$ MHz, and $\chi_{ab} = \chi_{ac} = 0$.

III. MICROWAVE SPECTRUM

The microwave spectrum of diethyl amine was assumed to be similar to the spectrum of dimethyl amine extensively studied by Wollrab and Laurie.⁴ The molecule has the same symmetry, a similar ratio of the dipole moment components and also tunneling splittings arising from an inversion motion at the nitrogen atom were expected. Moreover, all lines should show a ^{14}N quadrupole hyperfine structure on the order of 0.5 MHz and a smaller additional splitting due to the internal rotation of two methyl groups. From the dipole moment components obtained from the *ab initio* calculations the c -type spectrum was estimated to be by a factor of 4 stronger

than the b -type spectrum, whereas a -type lines cannot be observed at all.

A. Overall rotation and nitrogen inversion tunneling

As mentioned before all heavy atoms are located almost within one plane. The inversion motion can be considered as a tunneling of the amino hydrogen from one energy minimum at one side of this plane to an equivalent minimum on the other side of the plane (see equilibrium structure versions I and II in Fig. 1). This causes the lowest vibrational level ($v = 0$) to split into a lower symmetric (+) sublevel and a higher antisymmetric (-) sublevel. In the equilibrium geometry the c axis is only approximately perpendicular to the plane containing the heavy atoms and if the hydrogen atom moves during the tunneling process, the principal axes of inertia are not conserved. The sign of the c dipole component is exchanged (compare Fig. 1) during the tunneling motion causing the selection rules $+ \leftrightarrow -$ and $- \leftrightarrow +$ for the c -type transitions. The sign of the b dipole component does not change upon inversion and the selection rules $+ \leftrightarrow +$ and $- \leftrightarrow -$ are obtained for b -type transitions. In the case of dimethyl amine the separation between the (+) and the (-) sublevel was ~ 1.323 GHz causing the c -type lines to split into doublets separated by 2.646 GHz. The selection rules for the b -type transitions predict these lines to be unsplit, however, due to Coriolis interaction a narrow splitting usually below 100 kHz is observed.

For the assignment a broadband scan in the range from 14.5 to 16.5 GHz was recorded (Fig. 2). As a first step a rigid rotor spectrum based on the rotational constants from the *ab initio* calculations was calculated. The b type Q-branch lines $J_{1,J-1} \leftarrow J_{0,J}$ (marked in blue in Fig. 2) were immediately identified and were used to improve the $A - (B + C)/2$ and the $B - C$ rotational constants. In a second step the center frequencies of the c -type Q-branch $J_{1,J} \leftarrow J_{0,J}$ were predicted. Since the inversion splitting was unknown at that time, the

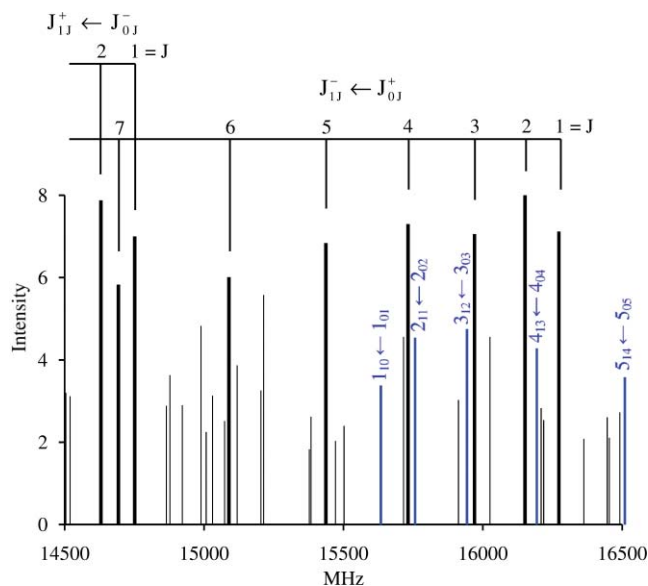


FIG. 2. Broadband scan of diethyl amine in the range of 14.5 – 16.5 GHz. Q-branch b type transitions are marked in blue. The c type transitions are shown as thick lines. They are split into two components due to proton tunneling.

calculated spectrum was shifted to higher frequencies and at an offset of 0.761 GHz the observed and calculated spectra matched. This was confirmed by shifting the calculated frequencies by the same offset to lower frequencies, where the transitions $1_{11}^+ \leftarrow 1_{01}^-$ and $2_{12}^+ \leftarrow 2_{02}^-$ were found. Therefore, the splitting of the rotational lines due to inversion was found to be 1.522 MHz.

B. ^{14}N Nuclear quadrupole coupling

All lines of the assigned c type Q-branch $J_{1,J} \leftarrow J_{0,J}$ appear as multiplets with a different number of lines. The two inversion components ($+ \leftarrow -$) and ($- \leftarrow +$) of the $1_{11} \leftarrow 1_{01}$ transition are sextets. For $J = 2$ to $J = 5$ septets were found and for $J > 5$ only triplets could be measured. Therefore, we attribute these splittings to ^{14}N hyperfine quadrupole coupling. It was surprising that even for $J = 5$ septets could be observed, since the intensity of the $F \leftrightarrow F + 1$ transitions should be only about 1.09% of the total multiplet intensity.

C. Methyl internal rotation

All components of the ^{14}N quadrupole hyperfine multiplets were split again into triplets. These splittings are on the order of 20 kHz, which is the same order of magnitude Fliege *et al.* have reported for ethyl fluoride.¹⁴ Therefore, we conclude that also in the case of diethyl amine the barrier should be on the order of 1171 cm^{-1} as in ethyl fluoride. The triplet structure is often found for molecules with two equivalent methyl groups with a high hindering potential.¹⁵ A typical spectrum is shown in Fig. 3.

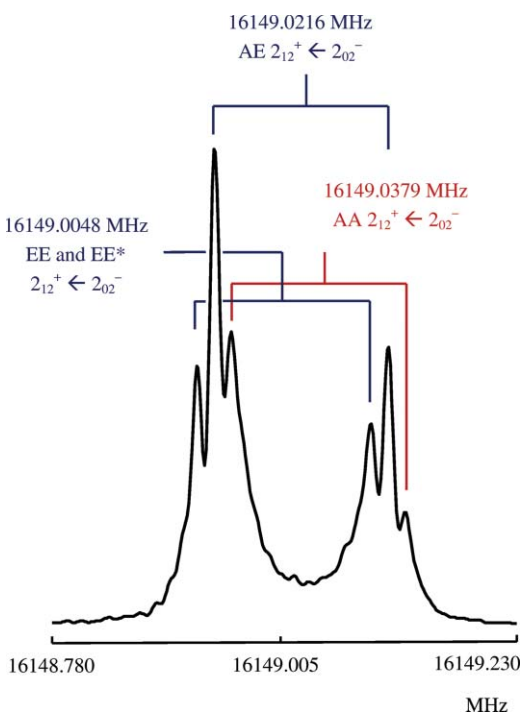


FIG. 3. The $F: 1 \leftarrow 2$ hyperfine component of the $2_{12}^- \leftarrow 2_{02}^+$ transition of diethyl amine with splittings due to internal rotation of two methyl groups. Doppler splittings are marked by brackets. For symmetry labels see Ref. 8.

IV. ANALYSIS AND DISCUSSION

After the structure of the spectrum was roughly understood, a global analysis of the overall rotation, the N inversion tunneling, and the ^{14}N nuclear quadrupole coupling was carried out using the program SPFIT written by Pickett.¹⁶ For this purpose the effective Hamiltonian

$$H = \sum_{v=0}^1 |v\rangle (H_R + H_{\Delta}^v + H_{NQ}(\chi_a, \chi_{bb} - \chi_{cc})) \langle v| + (|0\rangle \langle 1| + |1\rangle \langle 0|)(H_C + H_{NQ}(\chi_{bc})), \quad (1)$$

was used. $|0\rangle$ and $|1\rangle$ represent the symmetric (+) and the antisymmetric (−) inversion state, respectively. The notation is similar to that used by Christen *et al.*¹⁷ The operator

$$H_R = A J_a^2 + B J_b^2 + C J_c^2 - \Delta_J J^4 - \Delta_{JK} J^2 J_a^2 - \Delta_K J_a^4 - \delta_J J^2 (J_+^2 + J_-^2) - \frac{1}{2} \delta_K [J_a^2, (J_+^2 + J_-^2)]_+, \quad (2)$$

with $J_{\pm} = J_b \pm i J_c$ and the anti-commutator $[\dots]_+$ describes the overall rotation and the centrifugal distortion in terms of Watson's A reduction in the I' representation.¹⁸ The rotational constants A , B , C , and the centrifugal distortion constants Δ_J , Δ_{JK} , Δ_K , δ_J , δ_K are assumed to be the same for both, the $|0\rangle$ and $|1\rangle$ state.

The inversion splitting between the $|0\rangle$ and $|1\rangle$ energy levels and its J and K dependence is expressed by the operator

$$H_{\Delta}^v = vE + \frac{1}{2}(-1)^v (E_J J^2 + E_K J_a^2 + E_2 (J_+^2 + J_-^2) + E_{JK} J^2 J_a^2). \quad (3)$$

The Coriolis coupling operator is connecting the $|0\rangle$ and $|1\rangle$ state. It is given by

$$H_C = F_{bc}(J_b J_c + J_c J_b). \quad (4)$$

Finally, the operator of nuclear quadrupole coupling has both diagonal and off-diagonal matrix elements in the inversion quantum number v . It is represented by the expression

$$H_{NQ} = \mathbf{V}^{(2)} \cdot \mathbf{Q}^{(2)}. \quad (5)$$

$\mathbf{V}^{(2)}$ and $\mathbf{Q}^{(2)}$ are the second rank irreducible tensor operators of the electric field gradient tensor and the nuclear quadrupole tensor, respectively. Details of treating nuclear quadrupole coupling using the irreducible tensor method is given in Ref. 19. Again, the nuclear quadrupole coupling constants χ_{fg} , $f, g \in \{a, b, c\}$ are assumed to be the same for both inversion states. Matrix elements associated with the diagonal coupling constants χ_{aa} and $\chi_{bb} - \chi_{cc}$ are also diagonal in the $|0\rangle$ and in the $|1\rangle$ state, respectively. The influence of the off-diagonal constant χ_{bc} is only a second-order effect associated with the operator $J_b J_c + J_c J_b$. Its matrix elements diagonal in the inversion quantum number are zero, but as in the Coriolis coupling operator H_C they are non-zero for matrix element connecting the $|0\rangle$ and $|1\rangle$ state.

TABLE I. Parameters describing the overall rotation, nitrogen inversion, and ^{14}N quadrupole coupling of diethyl amine.

Parameter	Unit	Obs.	Calc.	Obs. – Calc.
Overall rotation and centrifugal distortion				
A	GHz	17.61499170(11)	17.7066	–0.0916 (–0.52%)
B	GHz	2.103650248(49)	2.1051	–0.0015 (–0.07%)
C	GHz	1.981332501(47)	1.9831	–0.0018 (–0.09%)
Δ_J	kHz	0.23755(49)		
Δ_{JK}	kHz	–3.1638(25)		
δ_J	kHz	0.025850(44)		
Nitrogen inversion tunneling and Coriolis interaction				
E	MHz	760.77062(20)		
E_J	kHz	1.6114(64)		
E_{JK}	kHz	–0.4550(82)		
E_K	MHz	–0.059444(30)		
E_2	kHz	0.4602(48)		
F_{bc}	MHz	0.45747(28)		
^{14}N quadrupole coupling				
χ_{aa}	MHz	2.67576(37)	2.766	–0.090 (–3.4%)
$\chi_{bb} - \chi_{cc}$	MHz	4.34144(65)	4.818	–0.477 (–11.0%)
χ_{bc}	MHz	2.9199(92)	3.244	–0.324 (–11.1%)
Statistical information				
N^a		228		
σ^b	kHz	4.4		

^aNumber of hyperfine components in the fit.^bStandard deviation of the fit.

It should be noted that the absolute sign of the Coriolis coupling constant F_{bc} and the off-diagonal nuclear quadrupole coupling constant χ_{bc} cannot be obtained from the experiment because it depends on how the directions of the principal axes of inertia are defined. However, the quantity $\text{sign}(F_{bc})/\text{sign}(\chi_{bc})$, which might be called the relative sign, is well-defined. Constants associated with the operators $J_a J_b + J_b J_a$ and $J_a J_c + J_c J_a$ are zero because the proton tunneling in diethyl amine is restricted to the bc plane.

A list of all transitions included in the fit is given as supplementary material¹¹ (Table S-II). The fitted parameters and a comparison with *ab initio* calculations is shown in Table I. The parameter definition (*.par) file of the program SPFIT is also available as supplementary material¹¹ (Table S-III).

All rotational constants agree better than 0.6% with the values obtained by quantum chemical calculations at the MP2/6-311++G(*d,p*) level of theory. This agreement is surprisingly good because the *ab initio* data refer to the equilibrium geometry of the molecule whereas the experimental constants are obtained for the vibrational ground state and no corrections were made. The quartic centrifugal distortion constants Δ_J , Δ_{JK} , and δ_J could be accurately determined; they have a reasonable order of magnitude for this kind of molecules. The constants Δ_K and δ_K were strongly correlated with other parameters and could not be determined.

The most important constant associated with the inversion tunneling is the separation between the lowest ($v = 0$) symmetric and antisymmetric inversion energy levels E. The slight J and K_a dependence of the level separation is described with the constants E_J , E_{JK} , E_K , and E_2 . As in former stud-

TABLE II. Calculated energy levels and splittings of diethyl amine.

v	$E^+/(kJ/mol)$	$E^-/(kJ/mol)$	$(E^- - E^+)/(kJ/mol)$	$(E^- - E^+)/h$
0	3.402	3.403	0.001	761 MHz
1	9.880	9.899	0.019	46.6 GHz
2	15.423	15.816	0.393	
3	19.514	21.521	2.007	
4	24.617	27.732	3.115	
5	31.102	34.612	3.510	

Note $V_{\text{max}} = 18.31$ kJ/mol, 1 kJ/mol = 83.59347 cm^{-1} , $I_r = 1.013534$ $\text{u}\text{\AA}^2$, $\theta_{\text{min}} = 54.842^\circ$, and $F/G = 1.5$, $m_{\text{max}} = 20$.

ies on amines the constant E was used to determine the barrier to inversion using a double minimum potential. Here, we used a modified version of a potential proposed by Weeks, Hecht, and Dennison for ammonia²⁰ and also used by Penn and Boggs for the inversion tunneling in methyl ethyl amine.⁶ Details concerning the model and the method of calculation are given in Appendix A. For diethyl amine a barrier of 1531 cm^{-1} (18.31 kJ/mol) was found. Some splittings of higher tunneling levels ($v = 1, 2, \dots$) calculated with the same model are given in Table II. The shape of the double minimum potential and the inversion energy levels are shown in Fig. 4. It should be noted that all calculations of the inversion barrier strongly depend on the model potential and on the equilibrium geometry of the molecule. Therefore, the barrier determined might contain a rather large systematic error, however, it is useful if it is compared with inversion barriers of other amines determined by exactly the same method. The results for dimethyl amine, methyl ethyl amine, and diethyl amine are given in Table III. In all cases the equilibrium geometry was obtained by *ab initio* calculations at the MP2/6-311++G(*d,p*) level of theory. All inversion barriers obtained by the same method were found within the narrow range of 1480 ± 59 cm^{-1} (17.7 ± 0.7 kJ/mol), whereas the agreement between the barriers reported earlier is worse.

The Coriolis coupling constant is associated with the operator $J_b J_c + J_c J_b$ which has matrix elements connecting the (+) and (–) inversion state. In the case of diethyl amine the

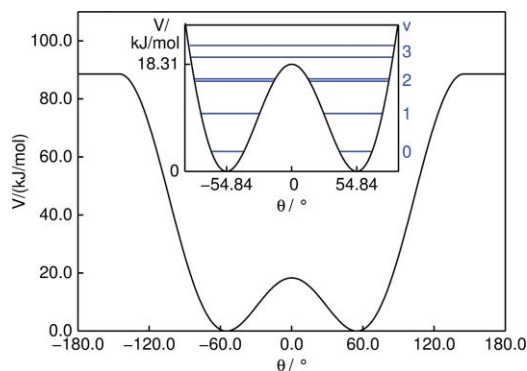


FIG. 4. The double minimum potential as defined in Appendix A used to describe the inversion tunneling at the nitrogen atom. The angle θ is the angle of the NH bond against the NCC plane. For the parameters see Table III. In the inset the angles for the calculated equilibrium geometries, the barrier height as determined from the $v = 0$ inversion splitting, and also the inversion levels (in blue) are shown. Each level marked by the v quantum number is split into a (+) and a (–) sublevel (see Table II).

TABLE III. Potential barrier of proton tunneling in some amines.

	$I_r/\text{u}\text{\AA}^2$	$\theta_{\min}/^\circ$	E/MHz	$V_{\max}/(\text{kJ/mol})$	V_{\max}/cm^{-1}
Dimethyl amine	1.000681	54.162	1323.0	17.17 ^a , 18.4(46) ⁴	1435 ^a , 1538(385) ⁴
Methyl ethyl amine	1.007155	54.528	990.5	17.77 ^a , 21.7 ⁶	1485 ^a , 1814 ⁶
Diethyl amine	1.013534	54.842	760.771	18.31 ^a	1531 ^a

^aThis work.

determination of F_{bc} is mainly due to a near degeneracy of the energy levels 3_{12}^+ and 3_{13}^- (Fig. 5). These levels are separated by only 27.5 MHz. Moreover, the near degeneracy causes a perturbation in the ^{14}N quadrupole coupling splitting associated with one of these levels. An example is shown in Fig. 6, where for the same rotational but different inversion transitions different hyperfine patterns appear. It should be noted that also in other amines such degeneracies are found, e.g., in ^{15}N -dimethyl amine the 1_{10}^+ and the 1_{11}^- level are separated by 66 MHz and by 204 MHz for the normal species.⁴ However, these values are much bigger and in the case of ^{14}N -dimethyl amine no perturbation of the nuclear quadrupole hyperfine structure has been reported.

The ^{14}N quadrupole coupling constants obtained from the global fit may be directly compared to the *ab initio* results. Here the deviation of the χ_{aa} constant is only -3.4% . In contrast, the $\chi_{bb} - \chi_{cc}$ and the χ_{bc} constants both differ by -11% . These rather large deviations might have two reasons: (i) When the constants were calculated from the electric field gradient tensor as obtained by *ab initio* calculations, an *effective* ^{14}N nuclear quadrupole moment of 19.41 mb was used. This value depends on the method and basis set and might be not suitable in this case. (ii) The $\chi_{bb} - \chi_{cc}$ and the χ_{bc} constants are averaged under the influence of the inversion tunneling. The χ_{aa} constant is not affected by this aver-

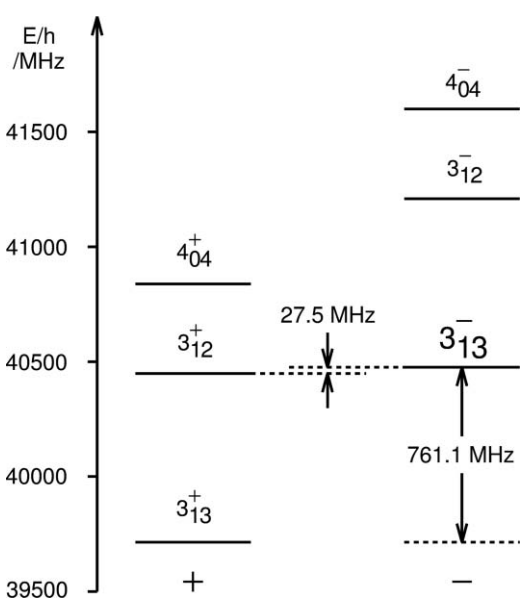


FIG. 5. Energy level diagram showing the near degenerate 3_{12}^+ and 3_{13}^- levels (27.5 MHz) and the inversion splitting of the 3_{13} level (761.1 MHz) into a symmetric (+) and an antisymmetric (-) inversion state. E/h is the rotation-inversion energy in frequency units.

aging process since the tunneling path of the proton is located in the bc plane.

The quadrupole constants were transformed into its principal axes. This allows for comparison with other amines. The results are shown in Table IV. The χ_{zz} value of -4.97626 MHz found for diethyl amine is in excellent agreement with $\chi_{zz} = -5.05$ MHz reported for dimethyl amine. The corresponding absolute values of ammonia and primary amines are usually lower, those of tertiary amines are slightly higher. Unfortunately, in some cases the accuracy of the reported coupling constants is not sufficient for a more detailed comparison. In Fig. 7, the orientation of the principal axes of the coupling tensor relative to the principal axes of inertia is shown. The z axis of the coupling tensor points in a direction where the maximum charge density of the nitrogen lone pair is expected. This also agrees nicely with the direction of the calculated dipole moment vector.

To determine the barrier to internal rotation, some selected c -type transitions showing torsional splittings (also that one in Fig. 3) were fitted with the program XIAM.²¹ Here, the splittings $\nu_{EE} - \nu_{AA}$, $\nu_{EE} - \nu_{AE}$, and $\nu_{EE} - \nu_{EE^*}$ instead of the absolute line frequencies were fitted. For the nomenclature of the torsional substates see Ref. 8. All other parameters such as the rotational constants and the angles between the internal rotor axes and the inertial axes were fixed and only the barrier to internal rotation was fitted. The result is given in Table V. A list of all fitted lines is available as supplementary material¹¹ (Table S-IV). The barrier to internal rotation was found to be ~ 1050 cm^{-1} which is in a good agreement with the barrier of about 1100 cm^{-1} of the methyl group found in

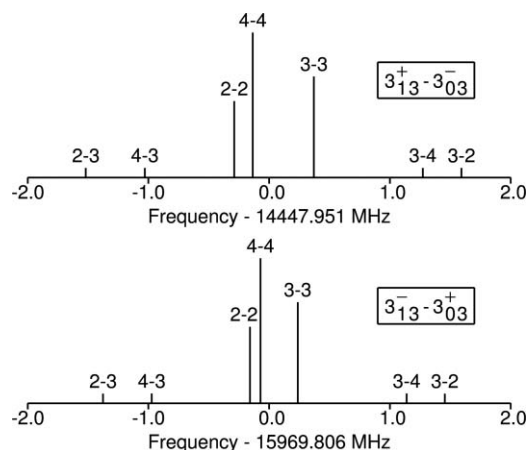


FIG. 6. ^{14}N quadrupole hyperfine structure of the $3_{13}^- \leftarrow 3_{03}^+$ transition. Different patterns arise from a perturbation of the 3_{13}^- level, which interacts with the only 27.5 MHz lower 3_{12}^+ level.

TABLE IV. Comparison of principal quadrupole coupling constants (in MHz) of ^{14}N in ammonia and in amines.

	χ_{xx}	χ_{yy}	χ_{zz}	η
Ammonia (Ref. 1)	2.0421	2.0421	-4.0842	0
Methyl amine (Ref. 2)	2.4136	1.9805	-4.3941	-0.099
<i>trans</i> -ethyl amine (Ref. 3)	2.93	1.75	-4.68	-0.25
Dimethyl amine (Ref. 4)	3.04	2.01	-5.05	-0.20
Diethyl amine ^a	2.67576	2.30050	-4.97626	-0.075
Trimethyl amine (Ref. 5)	2.74	2.74	-5.47	0
Quinuclidine ^b (Ref. 24)	2.5958	2.5958	-5.1915	0

Note: $\chi_{xx} \geq \chi_{yy} \geq \chi_{zz}$ (by definition). Asymmetry $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$.

^aThis work.

^bAlso called ABCO, 1-azabicyclo[2.2.2]octane.

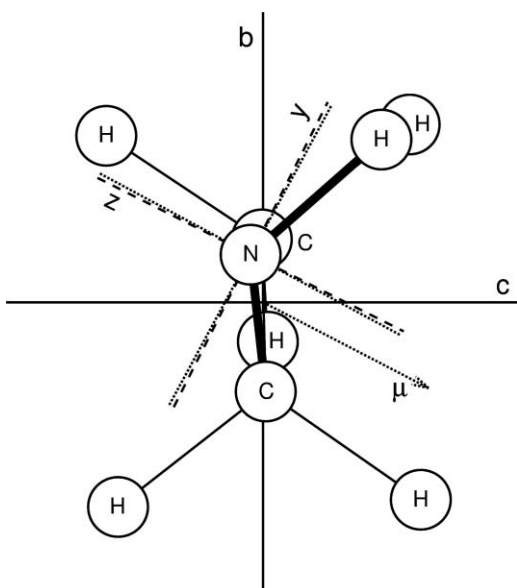


FIG. 7. Experimental and calculated (MP2/6-311++G(*d,p*)) principal axes x, y, z of the ^{14}N quadrupole coupling tensor. A part of the molecule is drawn as a projection on the bc plane. The bonds of the atoms directly bonded to the N atom are drawn as thick lines. The theoretical axes of the coupling tensor and also the theoretical dipole moment vector μ are dotted, the experimentally determined axes are dashed.

TABLE V. Parameters describing the internal rotation of two methyl groups of diethyl amine.

Parameter	Unit	Value
V_3	kJ/mol	12.5816(68)
	cm^{-1}	1051.74(57)
	GHz	31530(17)
I_α	$u\text{\AA}^2$	3.172 (fixed) ^a
$\angle(i_1, a)$	deg	35.85 (fixed) ^a
$\angle(i_2, a)$	deg	144.15 (fixed) ^{a, b}
$\angle(i_1, b) = \angle(i_2, b)$	deg	125.84 (fixed) ^a
$\angle(i_1, c) = \angle(i_2, c)$	deg	90.87 (fixed) ^a
N^c		48
σ^d	kHz	0.7

^aCalculated from structure optimized at the MP2/6-311++G(*d,p*) level.

^b $\angle(i_2, a) = 180^\circ - \angle(i_1, a)$ (due to symmetry).

^cNumber of torsional splittings.

^dStandard deviation of the fit.

ethyl fluoride¹⁴ and ethyl acetate,²² but much higher than the value of 772 cm^{-1} found in diethyl ketone.⁸ The reason for a lower barrier in diethyl ketone might be due to the inductive effect of the carbonyl group.

V. CONCLUSION

From the microwave spectrum of diethyl amine as recorded under molecular beam conditions molecular parameters were determined which allowed to reproduce the observed spectrum within experimental accuracy. The analysis was carried out using an effective Hamiltonian accounting for overall rotation, centrifugal distortion, nitrogen inversion, and ^{14}N nuclear quadrupole coupling. In contrast to previous work on dimethyl amine⁴ and methyl ethyl amine⁶ the inversion splittings of diethyl amine were described with molecular parameters instead of reporting the splitting of each single rotational transition.

From the inversion splittings of diethyl amine and those splittings reported for dimethyl amine and methyl ethyl amine the barriers to nitrogen inversion were calculated. This analysis was based on a simple model potential and on geometry parameters obtained by the same *ab initio* methods and basis sets for all three molecules. As a result, the inversion barriers were found consistently in a range of $1480 \pm 59\text{ cm}^{-1}$ ($17.7 \pm 0.7\text{ kJ/mol}$), and to increase monotonically in the chemical sequence dimethyl \rightarrow methyl ethyl \rightarrow diethyl amine.

Due to a near degeneracy of the 3_{13}^- and the 3_{12}^+ levels, which are separated by an energy difference of only 27.5 MHz, it became possible to determine the complete ^{14}N quadrupole coupling tensor. Thereby, also its principal axes could be determined without additional information from isotopic substitution. This is interesting because the z axis of the coupling tensor might be associated with the direction of the lone pair at the nitrogen atom. By comparison with the results of *ab initio* calculations the influence of vibrational averaging due to the nitrogen inversion could be identified.

Finally, due to the inherently high resolution of MB-FTMW spectroscopy narrow splittings due to internal rotation of the methyl groups were resolved and analyzed to give the torsional barrier of $1051.74(57)\text{ cm}^{-1}$ ($12.5816(68)\text{ kJ/mol}$).

This work is also considered as a reference for future studies to be carried out on other amines. Most parameters have been determined with a higher accuracy compared to the studies on dimethyl amine and methyl ethyl amine. Again, this is mainly due to the inherently high resolution of the MB-FTMW spectroscopy, a method which was not available at the time the older studies were carried out. It is also due to the availability of the easy to use and extremely flexible programs SPFIT and SPCAT by Pickett. Finally, it is due to a perturbation between two rotorsional energy levels. Such perturbations are also found in the other amines, but there the energy levels do not come as close together as in diethyl amine. However, it is believed that remeasurement and reanalysis of the spectra of the other amines would significantly improve their molecular parameters.

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APPENDIX A: PROTON TUNNELING

In order to obtain the hindering barrier from the observed nitrogen inversion splitting a model potential was chosen, since the exact potential and the tunneling path is usually not known. Several double minimum potentials have been described, e.g., that of Manning²³ or that of Weeks, Hecht, and Dennison.²⁰ The latter one has already been used by Penn and Boggs for the inversion tunneling in methyl ethyl amine⁶ and it will also be used here with slight modifications concerning the boundaries and the potential offset. The potential is assumed to be periodic in 2π :

$$V(\theta) = \frac{F^2}{4G} + 2G - 2F \cos \frac{\theta}{L} + 2G \cos \frac{2\theta}{L} \quad \text{for} \quad -\pi L \leq \theta \leq \pi L, \quad (\text{A1})$$

$$V(\theta) = \frac{F^2}{4G} + 2F + 4G \quad \text{for} \quad \begin{cases} -\pi \leq \theta < -\pi L \text{ and} \\ \pi L < \theta < \pi \end{cases}. \quad (\text{A2})$$

The parameter L is determined by the angles θ_{\min} , where the potential is $V(\theta_{\min}) = 0$,

$$\cos \frac{\theta_{\min}}{L} = \frac{F}{4G}. \quad (\text{A3})$$

F and G are positive parameters. Following the method of Penn and Boggs,⁶ they were fixed at a constant ratio of $F/G = 1.5$. However, the following expressions hold also for the general case of arbitrary F/G ratios. The height of the inversion barrier can be expressed as

$$V_{\max}(\theta = 0) = \frac{F^2}{4G} + 4G - 2F. \quad (\text{A4})$$

With this potential the Hamiltonian has the same form as in Ref. 20:

$$H = -D \frac{d^2}{d\theta^2} + V(\theta). \quad (\text{A5})$$

The parameter D is defined by

$$D = \frac{\hbar^2}{2I_r}, \quad (\text{A6})$$

with the reduced moment of inertia I_r , which refers to the rotation of the amine H atom on a circular path around the N atom against the molecular frame. Likewise, D can be expressed in frequency units by the rotational constant $D_r = D/h$.

The Hamilton matrix was set up in the basis of the planar rotor wave functions

$$|m\rangle = \sqrt{\frac{1}{2\pi}} e^{im\theta}, \quad i^2 = -1, \quad (\text{A7})$$

and truncated at a certain $m = m_{\max}$. The matrix elements are given by

$$\begin{aligned} \langle m|H|n\rangle &= Dm^2 f(n-m, \pi) \\ &+ \left(\frac{F^2}{4G} + 2G\right) f(n-m, \pi L) \\ &- F \left[f\left(n-m + \frac{1}{L}, \pi L\right) + f\left(n-m - \frac{1}{L}, \pi L\right) \right] \\ &+ G \left[f\left(n-m + \frac{2}{L}, \pi L\right) + f\left(n-m - \frac{2}{L}, \pi L\right) \right] \\ &+ \left(\frac{F^2}{4G} + 2F + 4G\right) \\ &\times [f(n-m, \pi) - f(n-m, \pi L)] \end{aligned} \quad (\text{A8})$$

with

$$f(r, A) = \frac{1}{2\pi} \int_{-A}^A e^{ir\theta} d\theta = \begin{cases} \frac{1}{\pi} A & \text{if } r = 0 \\ \frac{1}{r\pi} \sin rA & \text{if } r \neq 0 \end{cases}. \quad (\text{A9})$$

The energy eigenvalues were obtained by diagonalization of the Hamilton matrix using the Jacobi method. The eigenvalues are labeled by 0^+ , 0^- , 1^+ , 1^- , 2^+ , 2^- , ... in an ascending order of energy.

APPENDIX B: SUPPLEMENTARY MATERIAL

There is supplementary material¹¹ available for this paper. Table S-I contains the nuclear coordinates of diethyl amine in the principal axes of inertia as calculated at the MP2/6-311++G(d,p) level of theory. In Table S-II a frequency list of all assigned transitions of diethyl amine is given. Table S-III contains a part of the parameter definition (*.par) file of the program SPFIT used for fitting the overall rotation, the inversion tunneling, and the ¹⁴N quadrupole hyperfine structure. Finally, a list of all torsional components used to fit the internal rotation parameters of two methyl groups is given in Table S-IV.

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