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The effects of methyl internal rotation and ^{14}N quadrupole coupling in the microwave spectra of two conformers of N,N-diethylacetamide

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The gas phase structures and internal dynamics of N,N-diethylacetamide were determined with very high accuracy using a combination of molecular beam Fourier-transform microwave spectroscopy and quantum chemical calculations at high levels. Conformational studies yielded five stable conformers with C_1 symmetry. The two most energetically favorable conformers, conformer I and II, could be found in the experimental spectrum. For both conformers, quadrupole hyperfine splittings of the ^{14}N nucleus and torsional fine splittings due to the internal rotation of the acetyl methyl group occurred in the same order of magnitude and were fully assigned. The rotational constants, centrifugal distortion constants as well as the quadrupole coupling constants of the ^{14}N nucleus were determined and fitted to experimental accuracy. The V_3 potentials were found to be $517.04(13)\text{ cm}^{-1}$ and $619.48(91)\text{ cm}^{-1}$ for conformer I and II, respectively, and compared to the V_3 potentials found in other acetamides. Highly accurate CCSD(T) and DMC calculations were carried out for calculating the barriers to internal rotation in comparison with the experimentally deduced V_3 values.
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I. INTRODUCTION

Acetyl- and nitrogen-containing substances play an important role in chemistry and biology. Both aspects are present in acetamides. Amide bonds are fundamental structural elements in peptides, enzymes, and other biological systems. Basic knowledge on amides is therefore essential for many studies and developments in biology.

N,N-Diethylacetamide emerges in a condensation reaction between acetic acid and diethyl amine and is one of the smallest molecules containing an amide bond. Many molecules which have important influence on biological processes in human organisms contain N,N-diethylacetamide as a substructure (see Figure 1). For example, entacapone (**1**) is a drug used in the medical treatment for Parkinson's disease, which operates as an enzyme (catechol-O-methyl transferase (COMT)) inhibitor.¹ D-lysergic acid diethylamide (LSD) (**2**) is a well-known illegal drug and a very strong hallucinogen.² N-glycine-sulfonamide (**3**) acts as a potent and selective receptor antagonist for the neuropeptides orexin 1 and orexin 2, which play an important role in the regulation of the sleep-wake cycle.³ The structure and dynamics of N,N-diethylacetamide can thus reveal a part of the structures of larger biological molecules.

High resolution spectroscopic studies on small organic molecules have become the main interest of the molecular spectroscopy group in Aachen since the last years. Such molecules with their flexible structures and pronounced inter-

nal dynamics are not only interesting, but also important for fundamental investigation in physics and chemistry. Often, a combination of microwave spectroscopy and quantum chemical calculations is an excellent tool to determine the structure and dynamics of a molecule or a molecular system. This was shown in many cases studied and published in Aachen, for example in the most recent work on the natural substance linalool,⁴ one of the two main components of lavender oil, as well as current investigations in many other spectroscopy groups.⁵⁻⁷

A number of amides were studied by microwave spectroscopy so far, mainly by spectroscopy groups in Japan and Sweden. For example, the investigations on the simplest amides, formamide,⁸ as well as other larger amides such as N-methylformamide,⁹ N-vinylformamide,¹⁰ N-ethylformamide,¹¹ propionamide,¹² N,N-dimethylformamide,¹³ N-methylpropionamide,¹⁴ and some halogenated amides¹⁵ were reported. The rotational spectra of acetamide,^{16,17} *trans*- and *cis*-acetanilide,¹⁸ N-methylacetamide,^{19,20} and N,N-dimethylacetamide²¹ were also studied in the past. Detailed information on some of these molecules and their dynamical structures are given in the review article of Kawashima *et al.*²²

All of these molecules contain an acetyl methyl group, which undergoes internal rotation. The V_3 potential in acetamide is reported to be only 24.3 cm^{-1} , much lower than those found for other acetyl methyl groups for example in esters like methyl acetate (101.7 cm^{-1}),²³ isopropenyl acetate (135.3 cm^{-1})²⁴ or in ketones such as acetone (264.7 cm^{-1})^{25,26} or ethyl methyl ketone (181.5 cm^{-1}).²⁷ It is remarkable that the potential changes significantly when a hydrogen atom in the amide group is substituted by a methyl group, e.g., 73.5 cm^{-1} was found for

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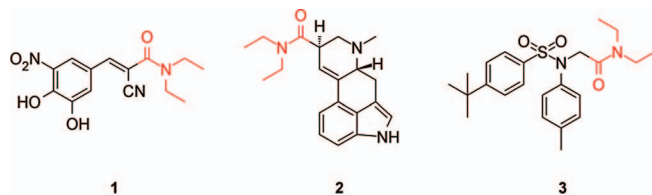


FIG. 1. Examples of biological molecules containing N,N-diethylacetamide as a substructure. (1) Entacapone, (2) LSD (D-lysergic acid diethylamide), and (3) 2-[(4-tert-butyl-benzene-sulfonyl)-p-tolyl-amino]-N,N-diethylacetamide.

N-methylacetamide.^{19,20} In *trans*-acetanilide, Caminati *et al.* reported on a V_3 potential of about 50 cm^{-1} which was determined from the pseudo inertial defect.¹⁸ By substitution of both hydrogen atoms in the amide group by two methyl groups, the potential increases by one order of magnitude. In N,N-dimethylacetamide, the V_3 potential of the acetyl methyl group was determined to be 677 cm^{-1} .²¹ Since it is a closely related molecule of N,N-diethylacetamide, we expected the V_3 potential of N,N-diethylacetamide to be similar. The splittings due to internal rotation are thus estimated to be in the order of a few hundreds of kHz and should be resolvable with the resolution of 2 kHz of our spectrometer in Aachen. Since the determination of the V_3 potentials in N,N-dimethylacetamide was stated to be ambiguous, some higher level theoretical calculations were carried out for N,N-diethylacetamide, in particular Diffusion Quantum Monte Carlo (DMC) and Coupled Cluster (CC) calculations. The V_3 potentials of the two ethyl methyl groups are expected to be higher than 1000 cm^{-1} and cannot be resolved in the microwave spectrum, similar to the case of triethyl amine.²⁸

In many previous studies on nitrogen containing molecules carried out in Aachen such as diethyl amine,²⁹ triethyl amine,²⁸ quinuclidine,³⁰ and morpholine,³¹ hyperfine splittings in the order of 0.5–1.0 MHz were observed due to the electric quadrupole moment of the ^{14}N nucleus. Therefore, we expected hyperfine splittings in the order of a few hundreds of kHz for N,N-diethylacetamide, which are in the same order of magnitude as the internal rotation fine splittings of the acetyl methyl group.

II. QUANTUM CHEMICAL CALCULATIONS

A. Conformational analysis

The conformational analysis was carried out at the second order Møller-Plesset perturbation theory and the basis set 6-311++G(d,p) using the program GAUSSIAN.³² This

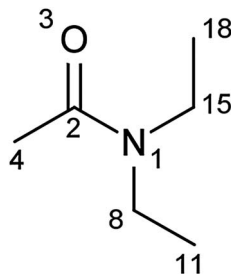


FIG. 2. N,N-diethylacetamide. Only the heavy atoms are numbered.

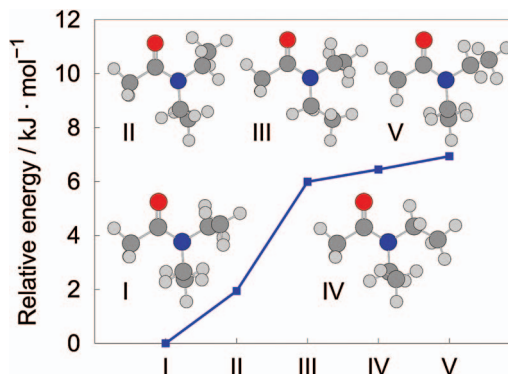


FIG. 3. Five stable conformers of N,N-diethylacetamide (named according to their order in energy) calculated at the MP2/6-311++G(d,p) level of theory. The energy values are relative to the most stable conformer I (-365.4789 hartree). All conformers have C_1 symmetry and exist as enantiomeric pairs. For each conformer, only one enantiomer is indicated.

level of theory was chosen because it yielded reasonable rotational constants in many previous studies in the spectroscopic community.^{33–36} The starting geometries were defined by varying three dihedral angles $\theta_1 = (C_4, C_2, N_1, C_8)$, $\theta_2 = (C_2, N_1, C_8, C_{11})$, and $\theta_3 = (C_2, N_1, C_{15}, C_{18})$ in a step width of 60° (for atom numbers see Figure 2). Due to the planarity of the acetyl group ($C_4-C_2=O_3$), only a rotation of θ_1 to 0° , 60° , and 120° was necessary, whereby $3 \times 6 \times 6 = 108$ starting geometries were created. The rotation of θ_1 to -60° , -120° , and 180° was omitted because it would lead to enantiomers which cannot be distinguished with our experimental method.

From the 108 starting geometries five stationary points on the potential energy surface could be found. Frequency calculations were carried out and yielded no imaginary frequencies, i.e., the optimized geometries are located in real energetic minima. The energies relative to the most stable conformer (conformer I) are indicated in Figure 3. Energy values, rotational constants, and dipole moment components of all conformers are summarized in Table I.

Conformer I (shown in Figure 4) is calculated to be the most stable conformer and expected to be observed in the microwave spectrum under molecular beam conditions. Conformer II is 1.9 kJ mol^{-1} higher in energy and might therefore also be present in the spectrum. In conformer I and II, all heavy atoms except C_{11} and C_{18} of the ethyl groups are almost located in a plane. In Conformer I the two ethyl groups are tilted out of this plane against each other by the same angle of approximately 110° , whereas in conformer II they are

TABLE I. Energy values, rotational constants, and dipole moment components of the stable conformers of N,N-diethylacetamide calculated at the MP2/6-311++G(d,p) level of theory. Relative energies are given in kJ mol^{-1} , rotational constants A , B , C are given in GHz, and dipole moment components are given in D.

	Rel. E	A	B	C	$ \mu_a $	$ \mu_b $	$ \mu_c $
I	0.0	2.072	1.939	1.159	3.489	2.134	1.465
II	1.9	2.207	1.915	1.188	3.024	3.037	0.491
III	6.0	2.404	1.727	1.145	2.997	2.784	1.109
IV	6.4	2.461	1.674	1.155	2.193	3.423	1.259
V	6.9	2.178	1.946	1.216	1.096	4.041	0.936

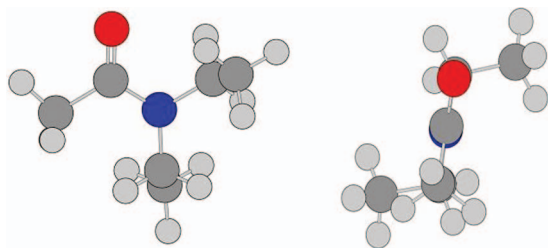


FIG. 4. The optimized geometry of conformer I of N,N-diethylacetamide calculated at the MP2/6-311++G(d,p) level of theory (left: front view and right: side view). The two ethyl groups are tilted out of the N–C=O plane against each other by the same angle of approximately 110° .

tilted out in the same direction, as presented in Figure 5. This more sterically hindered orientation explains the higher energy of conformer II. The Cartesian coordinates of conformer I and II in the principal axis system are available in Table S-I in the supplementary material.³⁷ In Table S-II, energy values and rotational constants optimized at different levels of theory are given for conformer I. Conformer III, IV, and V are about 6 kJ mol^{-1} higher in energy. From our experience, they cannot be observed under our molecular beam conditions. In these conformers, the C_8 and C_{15} atoms are out of the $C_4-C_2-O_3-N_1$ plane.

B. Methyl internal rotation

The barriers to internal rotation of the acetyl methyl group of conformer I and II were determined by standard B3LYP and MP2 as well as highly accurate CCSD(T) and DMC methods. To calculate the rotational barrier, the methyl group was rotated out of the equilibrium geometry while the rest of the molecule was free in relaxation. The molecular geometries for the DMC single point calculations were obtained at the B3LYP/aug-cc-pVTZ level of theory. All geometry optimizations were performed with the program GAUSSIAN. For the DMC calculations, a Salter-Jastrow ansatz was used,

$$\psi = e^U \Phi_{SD}, \quad (1)$$

where Φ_{SD} is a single Slater determinant and U is a correlation function first used by Schmidt and Moskowitz³⁸ that includes electron-electron, electron-nucleus, and electron-electron-nucleus terms. The Slater determinant was composed of Kohn-Sham orbitals generated with a B3LYP/cc-pVTZ sin-

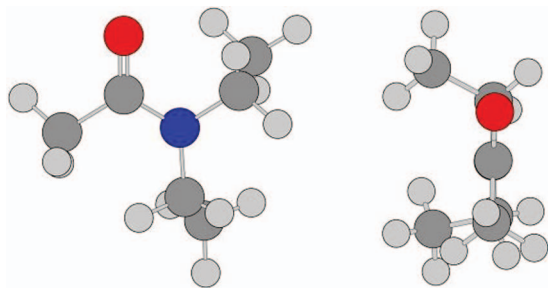


FIG. 5. The optimized geometry of conformer II of N,N-diethylacetamide calculated at the MP2/6-311++G(d,p) level of theory (left: front view and right: side view). The two ethyl groups are tilted out of the N–C=O plane in the same direction.

TABLE II. B3LYP, MP2, CC, and DMC rotational barriers for conformers I and II in kJ mol^{-1} . Values are given with one standard uncertainty in parentheses.

	C.I	C.II
B3LYP/cc-pVTZ//B3LYP/cc-pVTZ	4.0	
B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	4.0	4.4
B3LYP/CBS//B3LYP/cc-pVTZ	3.9	
MP2/cc-pVTZ//MP2/cc-pVTZ	4.5	
MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ	4.6	
MP2/CBS//MP2/cc-pVTZ	4.4	
CCSD(T)/cc-pVTZ//B3LYP/aug-cc-pVTZ	4.6	5.1
CCSD(T)/cc-pVTZ//MP2/aug-cc-pVTZ	4.5	
DMC//B3LYP/aug-cc-pVTZ	4.4(4)	

gle point calculation. All B3LYP, MP2, and CC single point calculations of this work were also carried out with the program GAUSSIAN. For the sake of clarity, the calculation level is given in the form *single point calculation level // geometry optimization level*. The parameters of the correlation factor U were optimized with respect to the energy.³⁹ The DMC energies are extrapolated to zero time step in the fixed node approximation.⁴⁰ The DMC calculations were carried out with the program AMOLQC.⁴¹ For B3LYP and MP2, an extrapolation of the energy to the complete basis set (CBS) was performed using Eq. (2) of Ref. 42 and cc-pVXZ basis sets up to $X = 5$. All energies are stationary points of the potential energy surface. Transition states of the methyl rotation were confirmed with frequency analyses.

Recent investigations on a similar level of theory showed for a series of smaller molecules that the current approach leads to agreement with experimental data within about 0.5 kJ mol^{-1} ,⁴³ which is the reason why it was chosen for the present investigation. The results for the B3LYP, MP2, CCSD(T), and DMC calculations are given in Table II.

C. ^{14}N nuclear quadrupole coupling

A hyperfine structure can be observed in the rotational spectrum if the spin of the nucleus is bigger than $1/2$ due to the electric quadrupole coupling. This effect appears in the spectra of all amides due to the nuclear spin $I = 1$ of the ^{14}N nucleus. The origin of the quadrupole coupling is the interaction of the electric nuclear quadrupole moment with the electric field gradient (EFG) at the site of the nucleus, which causes hyperfine splittings of the rotational lines. The order of magnitude of those splittings depends not only on the electric quadrupole moment of the coupling nucleus but also on the EFG. We thus carried out EFG calculations to get starting values for the hyperfine structure analysis. In some previous studies on amines,²⁸ EFG calculations of Bailey at the B3PW91/6-311+G(d,p)//MP2/6-311+G(df,pd) level of theory using the correction factor of eQ/h of $4.5617(43) \text{ MHz/a.u.}$ ⁴⁴ yielded quadrupole coupling constants which are in almost exact agreement with the experimental values. Thus, EFG single point calculations based on structures optimized at different levels of theory were carried out. The results are summarized in Table III.

TABLE III. The calculated quadrupole coupling constants χ_{aa} and $\chi_{bb}-\chi_{cc}$ as well as their deviations to the experimental values (expt.) (in MHz) of the ^{14}N nucleus in N,N-diethylacetamide. The electric field gradient was calculated at the B3PW91/6-311+G(d,p) level of theory based on structures optimized with the MP2 method and different basis sets. Values are given with one standard uncertainty in parentheses.

	χ_{aa}	$\Delta\chi_{aa}$	$\chi_{bb}-\chi_{cc}$	$\Delta(\chi_{bb}-\chi_{cc})$
C.I / expt.	1.06868(58)		5.07830(82)	
6-311++G(d,p)	1.1121	0.0434	5.2096	0.1313
6-311++G(df,pd)	1.1090	0.0403	5.1727	0.0944
6-311+G(d,p)	1.1199	0.0512	5.2076	0.1293
6-311+G(df,pd)	1.1139	0.0452	5.1704	0.0921
C.II / expt.	1.49797(61)		6.2522(11)	
6-311++G(d,p)	1.5923	0.0943	6.3038	0.0516
6-311++G(df,pd)	1.5821	0.0841	6.2707	0.0185
6-311+G(d,p)	1.5964	0.0984	6.3031	0.0509
6-311+G(df,pd)	1.5843	0.0863	6.2694	0.0172

III. MICROWAVE SPECTROSCOPY

A. Experimental setup

The spectra were recorded using a molecular beam Fourier transform microwave (MB-FTMW) spectrometer in the frequency range from 2 GHz to 26.5 GHz, which is a modified version of the spectrometer described in Refs. 45 and 46. Due to the relatively low vapor pressure of 0.927 hPa (at 298 K) of N,N-diethylacetamide, the substance was carried by a pipe cleaner.⁴⁷ The pipe cleaner was soaked with the liquid substance and positioned directly in front of the nozzle where the substance was picked up by a constant stream of the helium carrier gas. The mixture is expanded into a vacuum chamber at a total pressure of 150 to 175 kPa. N,N-diethylacetamide was purchased from Merck Schuchardt OHG, Hohenbrunn, Germany, with a stated purity of 98 % and used without further purification.

At the beginning, a broadband scan was carried out in the frequency range from 9 to 15 GHz, where overlapping spectra were automatically recorded in a step width of 0.25 MHz. A typical scan is shown in Figure 6. In total, 75 molecular signals could be observed in this region. Almost all of them already appeared as multiplets in the scan mode due to the quadrupole splittings of the ^{14}N nucleus. High resolution measurements with an experimental resolution of approximately 2 kHz were carried out afterwards. Multiplets were found which contain splittings from three different effects: the fine splittings from internal rotation of the acetyl methyl group, the quadrupole hyperfine splittings, and splittings due to the Doppler effect. A typical spectrum in the high resolution mode is illustrated in Figure 7.

B. Spectrum analysis

1. Conformer I

The assignment was carried out in three steps. As a first step, the internal rotation and quadrupole coupling effects were neglected and the molecule was treated as a rigid rotor. Using the A, B, and C rotational constants calculated at the MP2/6-311++G(d,p) level of theory (see Sec. II A),

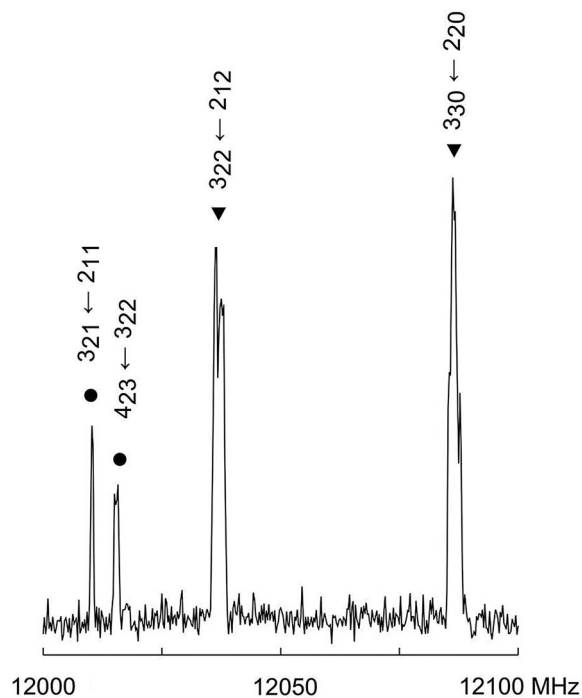


FIG. 6. A broadband scan of N,N-diethylacetamide in the frequency range from 12 000 to 12 100 MHz. The transitions of conformer I are marked with triangles and those of conformer II by circles. Additional splittings arise from the quadrupole coupling of the ^{14}N nucleus.

a first prediction was made using the program XIAM.⁴⁸ The predicted spectrum showed characteristic patterns which could be recognized from the spectrum in the scan mode. These lines enabled the initial assignment and fit. The rotational constants were improved and further *a*-, *b*-, and *c*-type

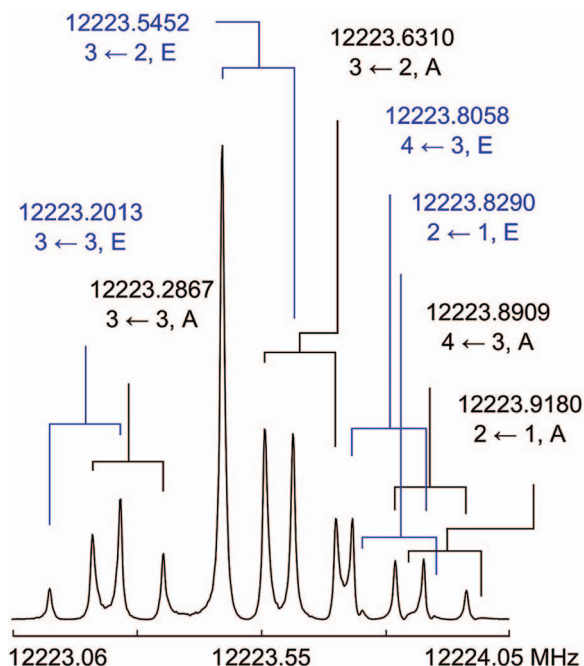


FIG. 7. The torsional and quadrupole components of the $3_{31} \leftarrow 2_{21}$ transition of conformer I of N,N-diethylacetamide. The experimental resolution is 2 kHz. Doppler doublets are marked by brackets. The A species is indicated in black and the E species in blue. The hyperfine transitions are given by $F' \leftarrow F$. For this spectrum, 800 decays were co-added.

transitions could be assigned. The calculated dipole moment in *c*-direction is smaller than those in *a*- and *b*-direction (see Table I). Accordingly, only five *c*-type transitions with small *J* quantum numbers, which showed considerably lower intensities, could be measured. In total, the rigid-rotor fit included 47 transitions with a standard deviation of 450 kHz.

In a second step, the rigid rotor model was extended by adding the quadrupole coupling effect. We began with this effect as, from our experience, the quadrupole coupling constants can be calculated almost exactly with EFG calculations using Bailey's method (see Sec. II C). Using the calculated quadrupole coupling constants at the B3PW91/6-311+G(d,p)//MP2/6-311++G(d,p) level of theory (see Table III), reasonable predictions of the hyperfine structures were carried out, which enabled the assignment of some hyperfine transitions of the $J = 3 \leftarrow 2$ *R*-branches. Afterwards, hyperfine components of all transitions in the rigid rotor fit could be included.

In the last step of the analysis, the internal rotation of the acetyl methyl group was taken into account. The initial value of the V_3 potential to internal rotation was set to 600 cm^{-1} , which is approximately the value of 677 cm^{-1} found in N,N-dimethylacetamide. The polar coordinates of the internal rotor axis in the principal axis system, δ and ε , were calculated from the optimized geometry obtained from quantum chemical calculations at the MP2/6-311++G(d,p) level of theory. δ is the angle between the internal rotation axis and the *a*-axis and ε is the angle between the *b*-axis and the projection of the internal rotation axis onto the *bc*-plane.

A reliable and unambiguous assignment of the quadrupole hyperfine and internal rotation fine structure was difficult because both effects cause splittings in the same order of a few tens to a few hundreds of kHz. The starting values played a significant role and an analysis of the splitting pattern had to be carried out very carefully. It should be mentioned that the hyperfine pattern appears twice in the spectrum, once for the A and once for the E species. Also the same A-E splittings appear for each transition in the quadrupole hyperfine structure, as shown in Figure 8. Here, the same A-E splitting of about 90 kHz can be found for the transitions $F' \leftarrow F$: $3 \leftarrow 3$, $3 \leftarrow 2$, $4 \leftarrow 3$, $2 \leftarrow 1$, and $2 \leftarrow 2$.

Finally, 345 torsional and hyperfine components could be assigned for conformer I and fitted using 12 molecular param-

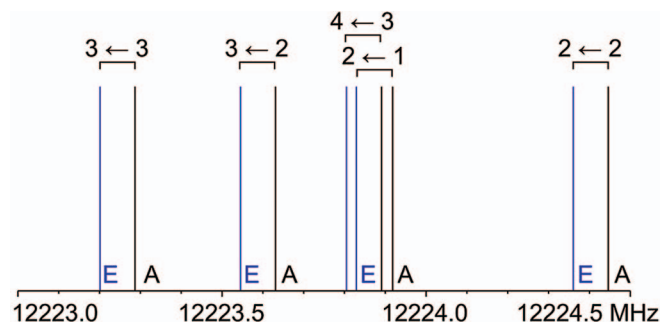


FIG. 8. The stick spectrum of the $3_{31} \leftarrow 2_{21}$ transition of conformer I of N,N-diethylacetamide. The same A-E splitting of about 90 kHz can be found for all hyperfine components $F' \leftarrow F$ and are marked with brackets. For the A species (black) and the E species (blue) the same hyperfine structure was found.

eters to a standard deviation of 1.4 kHz. All fitted parameters are given in Table IV. A list of all frequencies along with the residuals are available in Table S-III in the supplementary material.³⁷

2. Conformer II

After conformer I was assigned, a number of lines with significantly lower intensity remained in the scan, which belong to conformer II (1.9 kJ mol^{-1} higher in energy, see Sec. II A). The assignment process followed the three steps carried out for conformer I. At first, four transitions $5_{14} \leftarrow 4_{13}$, $5_{24} \leftarrow 4_{23}$, $5_{14} \leftarrow 4_{23}$, and $5_{24} \leftarrow 4_{13}$, which form a closed loop, were recognized in the spectrum. Afterwards, all remaining lines in the scan could be assigned to 29 rigid-rotor transitions of conformer II. In total, 247 torsional and hyperfine components were assigned for conformer II and fitted using 13 molecular parameters to a standard deviation of 1.6 kHz. The frequency list of all fitted transitions are available in Table S-IV in the supplementary material.³⁷

IV. RESULTS AND DISCUSSION

Using the program XIAM, 345 torsional and hyperfine components of conformer I and 247 components of conformer II of N,N-diethylacetamide were fitted by floating the rotational constants A , B , C , the centrifugal distortion constants D_J , D_{JK} , D_K , d_1 , d_2 , the V_3 potential, the polar coordinates of the internal rotation axis in the principal axis system δ and ε , and the quadrupole coupling constants χ_{aa} and $\chi_{bb}-\chi_{cc}$. The angles between the acetyl methyl group and the principal axes were derived from δ and ε . The moment of inertia I_α was kept fixed to $3.2 \text{ u}\text{\AA}^2$, corresponding to $F_0 = 158 \text{ GHz}$, a value often found for methyl groups. Since only torsional ground state transitions were measured, floating I_α led to a strong correlation with V_3 . The spectrum could be reproduced within the experimental resolution with a standard deviation of 1.4 kHz and 1.6 kHz for conformer I and II, respectively.

The experimental rotational constants are in reasonable agreement with the values from quantum chemical calculations at different levels of theory (Table S-II in the supplementary material).³⁷ Calculations at the MP2/6-31++G(d,p) level of theory yielded the most accurate rotational constants with deviations of 4 MHz, -7 MHz , and 1 MHz for the A , B , and C rotational constant, respectively. Also calculations at the MP2/6-31+G(d,p) and MP2/6-311++G(d,p) level of theory revealed rotational constants in a similar quality. A better agreement cannot be expected, as results from quantum chemical calculations refer to the equilibrium structure, whereas the experimental data yield rotational constants for the ground vibrational state and no corrections have been made. This accuracy is in good agreement with the calculations carried out for other molecules of similar size like linalool⁴ and ethyl methyl ketone.²⁷

The comparison of the calculated torsional barriers of the acetyl methyl group for conformer I showed a clear agreement at all different levels of theory. The MP2, CCSD(T), and DMC methods led to almost the same results, while DFT calculations produced slightly lower barriers. Because of the

TABLE IV. Rotational and torsional parameters from the program XIAM (obs.) compared to parameters calculated at the MP2/6-311++G(d,p) level of theory (calc.) for the observed conformers of N,N-diethylacetamide. Parameters are given with one standard uncertainty in parentheses. Watson's S reduction and I' representation were used.

	Unit	Conformer I			Conformer II		
		Obs.	Calc.	Obs.-Calc.	Obs.	Calc.	Obs.-Calc.
<i>A</i>	GHz	2.06594325(15)	2.072	−0.006	2.18125231(20)	2.207	−0.026
<i>B</i>	GHz	1.946434197(70)	1.939	0.007	1.933673393(99)	1.915	0.019
<i>C</i>	GHz	1.157141719(42)	1.159	−0.002	1.191944060(91)	1.188	0.004
<i>D_J</i>	kHz	0.3344(16)			0.8942(32)		
<i>D_{JK}</i>	kHz	0.0 ^a			−3.201(12)		
<i>D_K</i>	kHz	1.1214(90)			4.231(15)		
<i>d₁</i>	kHz	−0.1646(10)			−0.2884(19)		
<i>d₂</i>	kHz	−0.03149(30)			0.0535(12)		
<i>X_{aa}</i>	MHz	1.06868(58)	1.1121	−0.0434	1.49797(61)	1.5923	−0.0943
<i>X_{bb}−X_{cc}</i>	MHz	5.07830(82)	5.2096	−0.1313	6.2522(11)	6.3038	−0.0516
<i>F₀</i>	GHz	158.0 ^a			158.0 ^a		
<i>V₃</i>	GHz	15500.6(37)			18572(28)		
	cm ^{−1}	517.04(13)			619.48(91)		
	kJ mol ^{−1}	6.1852(15)	6.1 ^c	0.1	7.411(11)	6.8 ^c	0.6
<i>I_α</i>	uÅ ²	3.2 ^b			3.2 ^b		
<i>∠(i,a)</i>	deg	44.446(91)	48.07	−3.62	60.58(48)	67.73	−7.15
<i>∠(i,b)</i>	deg	50.634(99)	49.25	1.38	32.45(49)	25.57	6.88
<i>∠(i,c)</i>	deg	72.740(69)	69.10	3.64	77.53(20)	78.07	−0.54
<i>σ</i>	kHz	1.4			1.6		
<i>N^d</i>		345			247		

^aFixed value.

^bDerived parameter.

^cRigid rotor approach, see Sec. IV.

^dNumber of lines.

consistency of all results for conformer I, the calculations for conformer II were restricted to B3LYP and CCSD(T) calculations, where we expected the CCSD(T) result to be more reliable than the result obtained by B3LYP.

The experimental *V₃* potential was fitted to 517.04(13) cm^{−1} (6.1852(15) kJ mol^{−1}) and 619.48(91) cm^{−1} (7.411(11) kJ mol^{−1}) for conformer I and II, respectively. Comparing the experimental *V₃* values with the calculated rotational barriers, one can state significant differences of more than 2 kJ mol^{−1}, which cannot be explained with limitations of the electronic structure calculations. The diffuse functions in the basis set and the extrapolation to the CBS show no effect on the barrier. Due to the agreement of the DMC, MP2, and CCSD(T) results, no effect of higher order excitations is expected and, finally, the T1 diagnostics⁴⁹ confirms the lack of static correlation.

We assume that the difference between the calculated barrier and the experimental *V₃* value is due to the fact that a rigid rotor model for internal rotation is used in the fit of the microwave data whereas the calculated barrier is obtained from full geometry relaxation. To test this conjecture, we repeated the CCSD(T)/cc-pVTZ//B3LYP/aug-cc-pVTZ calculations with a fixed methyl rotor. For this purpose, all C-H and C-C bonds, C-C-H angles, as well as all H-C-C-H dihedral angles of the methyl group were averaged using the geometries of the minimum and the transition state of the rotation. Freezing the constructed methyl rotors, the geometry of the potential energetic minimum and the transition state were optimized. For the fixed methyl group, the barriers of conformer

I and II change to 6.1 kJ mol^{−1} and 6.8 kJ mol^{−1}, respectively. Taking only the geometries of the energetic minima or of the transition states as basis for the construction of the rigid rotors, the rotational barriers change by less than 0.05 kJ mol^{−1}. The calculated rotational barrier and the experimental *V₃* potential differ by 0.1 kJ mol^{−1} and 0.6 kJ mol^{−1} for conformer I and II, respectively.

For comparison, the same procedure was carried out for acetaldehyde and acetylfluoride, where excellent agreement with experimental data using relaxed methyl rotors was observed.⁴³ The introduction of rigid rotors for these systems did not change the methyl rotational barriers. The influence of a geometrically fixed methyl rotor seems to be compound specific and leads to good agreements between the calculated rotational barrier and experimental *V₃* potential. Hence, our future plan considers the investigation of different acetamides and the comparison to experimental results with respect to a rigid rotor.

The experimental *V₃* potential of conformer II matches the *V₃* potential of 677 cm^{−1} found for N,N-dimethylacetamide.²¹ In Ref. 21, an unambiguous determination of the *V₃* potential of the acetyl methyl group could not be made and two possible values, 677 cm^{−1} and 238 cm^{−1}, were given. The potential of 677 cm^{−1} was only supported by comparing with the results from quantum chemical calculations performed at the MP2/6-31G(d,p) level of theory. Our study on N,N-diethylacetamide strongly confirms the assignment for the *V₃* potential of the acetyl methyl group in Ref. 21.

From our experience, the V_3 potential of the acetyl methyl group is almost exactly the same for the three conformers of *n*-butyl acetate⁵⁰ and the two conformers of *n*-pentyl acetate.⁵¹ Therefore, we expected the same V_3 potential for the two conformers of *N,N*-diethylacetamide. Contrary to our expectation, the acetyl methyl V_3 potentials of conformer I and II differ by approximately 100 cm^{-1} . However, as mentioned in the introduction, the acetyl methyl V_3 potentials in acetamides often depends strongly on the substitutions at the other side of the amide bond and can vary in a very wide range from 24 cm^{-1} like in the case of acetamide up to 677 cm^{-1} like in *N,N*-dimethylacetamide. Significant changes in the V_3 potential could also be found, even when the hydrogen atoms in the amide group are only substituted by deuterium.⁵² Therefore, it is not surprising that the V_3 potential also depends on the configuration of the substitutions attached to the nitrogen atom.

The experimental angles between the internal rotor axis and the principal axes of conformer I and II differ by a few degrees from the calculated values optimized at the MP2/6-311++G(d,p) level of theory. The $\angle(i,b)$ angle of conformer I and the $\angle(i,c)$ angle of conformer II are in a good agreement with the experimental values. The differences of the other angles of about 4° and 7° for conformer I and II, respectively, are quite high comparing with other studies on internal rotation.^{50,53,54} However, fixing the values of the internal rotation angles in the fits to theoretical values yielded only minor differences and comparable standard deviations, which means that the fits are not extremely sensitive to these parameters.

The quadrupole coupling constants χ_{aa} and $\chi_{bb}-\chi_{cc}$ could be fitted with very high accuracy. The calculated values match the experimental ones almost exactly. The best results were obtained at the B3PW91/6-311+G(d,p)/MP2/6-311++G(df,pd) and B3PW91/6-311+G(d,p)/MP2/6-311+G(df,pd) level of theory for both conformers.

V. CONCLUSION

Using a MB-FTMW spectrometer in the frequency range from 2 to 26.5 GHz, the torsional fine structure and the quadrupole hyperfine structure in the rotational spectra of two conformers of *N,N*-diethylacetamide could be fully resolved and analyzed in a global fit with the program XIAM. The spectra could be reproduced within our experimental resolution using 12 fitted parameters for 345 lines with a ratio of 29 lines/parameter for conformer I and 13 fitted parameters for 247 lines with a ratio of 19 lines/parameter for conformer II. The spectroscopic work was supplemented by quantum chemical calculations.

The acetyl methyl group undergoes internal rotation with a V_3 potential of $517.04(13)\text{ cm}^{-1}$ and $619.48(91)\text{ cm}^{-1}$ for conformer I and II, respectively. The DMC and CC calculations for the relaxed rotor indicated a methyl rotational barrier which is about 2 kJ mol^{-1} lower than the experimental V_3 value, whereas the rigid rotor modification showed a very good agreement of 0.1 kJ mol^{-1} and 0.6 kJ mol^{-1} for conformer I and II, respectively.

The quadrupole coupling constants of the ^{14}N nucleus were determined with very high accuracy. EFG calculations

with Bailey's method could calculate the coupling constants almost exactly to the experimental values.

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