The Rotational Zeeman Effect in Acetone, its g-Tensor, its Magnetic Susceptibility Anisotropies and its Molecular Electric Quadrupole Moment Tensor; A High Resolution Microwave Fourier Transform Study

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Acetone is a molecule with an intermediate barrier for methyl- top internal rotation, and only molecules in the A_1A_1-state of the tunneling motion exhibit a rigid rotor spectrum. For this state we report the results of a rotational Zeeman effect study of acetone in exterior fields up to 20 kGauss (2 Tesla). From an analysis of the observed Zeeman splittings within the asymmetric top approximation the nonzero elements of the g-tensor and the magnetic susceptibility anisotropies were obtained as follows:

$$g_{aa} = -0.04379\ (8), \quad g_{bb} = -0.06611\ (5), \quad g_{cc} = -0.01481\ (7),$$

$2\,\xi_{aa} - \xi_{bb} - \xi_{cc} = -9.53\ (21)\ 10^{-6}\ \mathrm{erg\ G^{-2}\ mole^{-1}}$ and $2\,\xi_{bb} - \xi_{cc} - \xi_{aa} = 25.57\ (18)\ 10^{-6}\ \mathrm{erg\ G^{-2}\ mole^{-1}}$. The nonzero elements of the molecular electric quadrupole moment tensor were derived as

$$Q_{aa} = 2.77\ (13)\ \mathrm{DÅ}, \quad Q_{bb} = -4.59\ (10)\ \mathrm{DÅ} \quad \text{and} \quad Q_{cc} = 1.82\ (15)\ \mathrm{DÅ}.$$

Zeeman spectra were also recorded for seveal low-J transitions of molecules in the EE-state of methyl top tunneling (one top tunneling), and so far the same splittings have been found as for the A_1A_1-species.

Introduction

Acetone, $CH_3{-}C(O){-}CH_3$, is a molecule in which the internal rotation of the two methyl tops is hindered by a barrier of intermediate height. Even in the vibronic ground state, tunneling of the tops leads to a perturbation of the overall rotation and each rotational transition is split into a quartet. Figure 1 is intended to provide a general idea of these tunneling (or internal rotation) splittings. From them the barrier height can be deduced. The most recent value for the latter has been presented by Vacherand, van Eijck, Burie, and Demaison [1, 2], who have also studied several deuterated species and who could show conclusively that the equilibrium configuration of acetone has C_{2v}-symmetry with the inplane hydrogen of each top in cis position with respect to the oxygen. From their studies the barrier to CH_3-internal rotation has the value $V_3 = 760.82\ (14)$ cal mole^{-1} or $266.28\ (5)$ cm^{-1}. For earlier investigations see [3–5].

Our interest in a rotational Zeeman effect study was threefold. First of all we wanted to check an old prediction for the nonzero elements of the g-tensor and of the magnetic susceptibility tensor [6]. This prediction had essentially been based on additivity rules for the individual components of the molecular magnetic susceptibility tensor. These rules had been developed originally by T. Schmalz from Flygare's group at Urbana [7, 8] as an extension of Pascal's rules for the bulk susceptibilities. Additional input of the molecular structure [9] and of electronic ground state expectation values for the squares of the electron coordinates $\langle 0 | \sum a_e^2 | 0 \rangle$ etc. had also lead to a prediction of the g-tensor. Second we wanted to see whether CH_3-tunneling would lead to different Zeeman-patterns for molecules in different tunneling states. Last not least we wanted to use the rotational Zeeman effect for an experimental determination of the molecular electric quadrupole moment of the molecule. Together with the knowledge of the molecular electric dipole moment the knowledge of the molecular electric quadrupole moment is thought to be important for the understanding of the shapes of weakly bound van der Waals complexes. Furthermore acetone has been observed in

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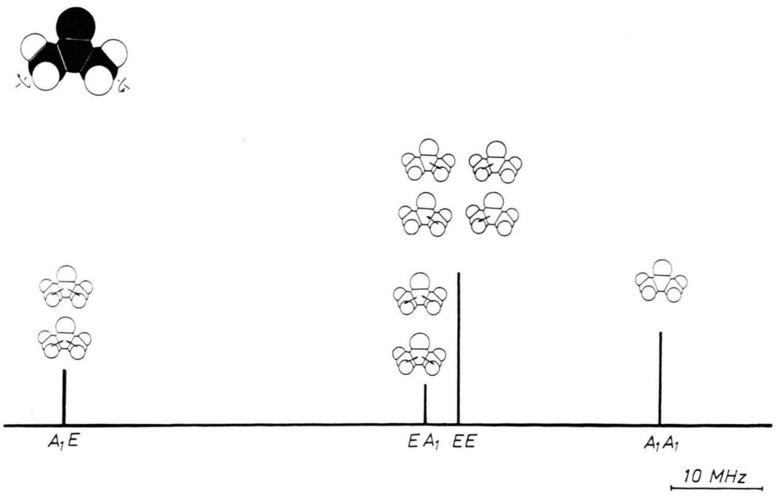

Fig. 1. In the vibronic states investigated here, the molecule is essentially locked in its shown equilibrium configuration. Yet tunneling of the two methyl tops leads to quartet splittings of the rotational transition as is shown in this bar spectrum, which corresponds to the $3_{21} \rightarrow 3_{12}$ rotational transition. The internal angular momentum due to tunneling is indicated by arrows. It is very small and the magnetic moment associated with it could not be detected with the available resolution. Proton spin statistics determines the relative intensities of the torsional satellites.

interstellar space [10] and its dipole and quadrupole moment might be also of interest for a more detailed understanding of ion/molecule reaction mechanisms in interstellar clouds.

Experimental and Analysis

The spectrometer used in the present investigation is basically the same as describd earlier in [11], but its frequency range has been extended to include the Ku-band (12.4 to 18 GHz). In-band rectangular brass waveguides were used as absorption cells. Typical sample pressures were around 1 mTorr and typical cell temperatures were close to −50 °C. As an example for the quality of the spectra obtained we present zero field and high field transient emission signals and the corresponding Fourier transform amplitude spectra for the $3_{21} \rightarrow 3_{12}$ rotational transition in Figs. 2 and 3. They arose from molecules in the non-tunneling A_1A_1-state of internal rotation. For the final determination of the zero field frequencies and of the Zeeman satellite frequencies we have used Haekel's computer program [12] in which the frequencies, amplitudes and phases, which are present in the transient emission signal are fitted to the latter by an iterative non linear least squares procedure.

In Table 1 we present some results. We also present observed Zeeman satellite frequencies for several rotational transitions of molecules in the EE-torsional state (just one top tunneling). The splittings are essentially the same as for the A_1A_1-species. Apparently the angular velocity associated with the tunneling is too small as to give rise to measurable extra magnetic moments, quite in analogy to the case of acetaldehyde, an other molecule with an intermediate barrier to internal methyl top rotation [13].

For the determination of the g-tensor elements and of the susceptibility anisotropies wer have used the Zeeman splittings observed for molecules in the non-tunneling A_1A_1-state of internal rotation, and we have applied the standard rigid rotor theory to fit the g-tensor elements and susceptibility anisotropies to the observed splittings. The effective rotational constants of the A_1A_1-species were used as additional input. (They determine the expectation values for the squares of the angular momentum operators J_a^2, J_b^2, and J_c^2 which enter into the theoretical expressions for the splittings (c.f. Chapter B in [6])). The results of the corresponding least squares fit are presented in Table 2. The sign of the g-values (only their relative signs are determined by the experiment) follows conclusively from the fact that the opposite choice of sign would lead to unreasonably large quadrupole moments (see below). Also given for comparison are the corresponding results obtained for the EE-torsional state. Neglecting tunneling they too were fitted to the observed Zeeman splittings by use of the standard rigid rotor theory albeit with a different set of rotational constants. We found that the rigid rotor theory fits the observed splittings surprisingly well. Originally we had expected that in the Zeeman splittings of the EE-species rotational transitions tunneling would lead to 10 to 30 kHz deviations from rigid rotor behaviour. This

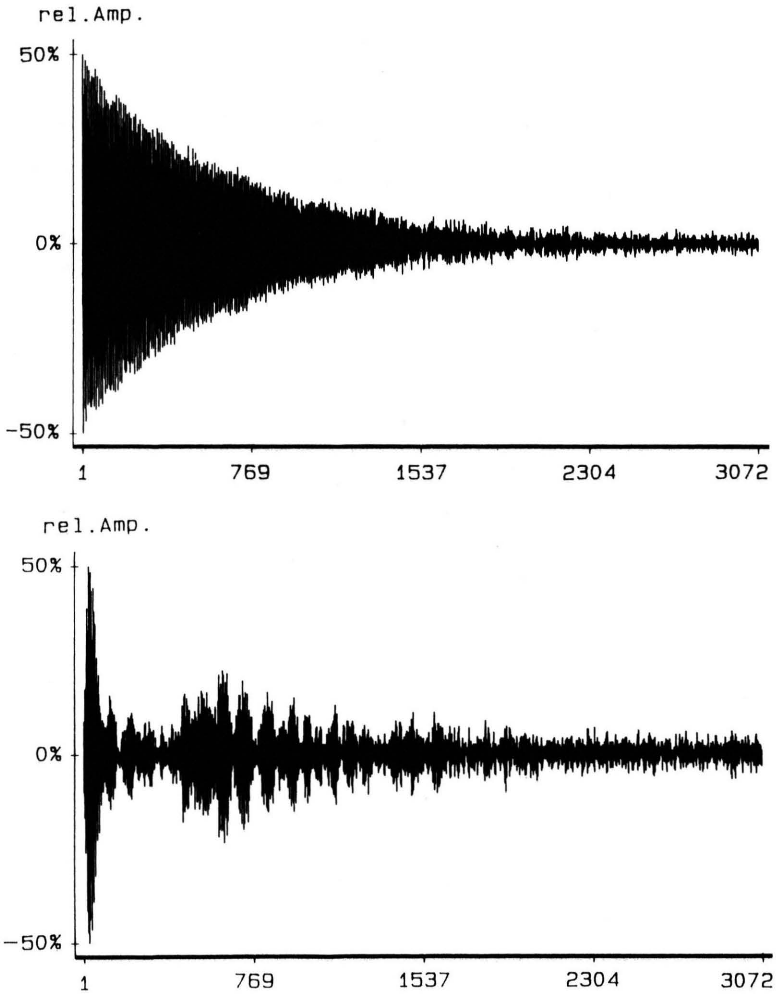

Fig. 2. Transient emission signals from the $3_{21} \rightarrow 3_{12}$ rotational transition of molecules in the A_1A_1 state of the CH_3-tunneling motion. The upper transient is observed with the magnetic field turned off. The lower transient is observed in a magnetic field of 17891 Gauss. Totals of 3.2768 10^6 (zero field case) and 98.304 10^6 (field-on case) transients were averaged up to obtain the signals presented here. From each transient emission 3072 data points were sampled at 10 ns intervals, which translates into an observation time of 30.72 µs. The gas pressure was about 1 mTorr and the temperature was about −50 °C.

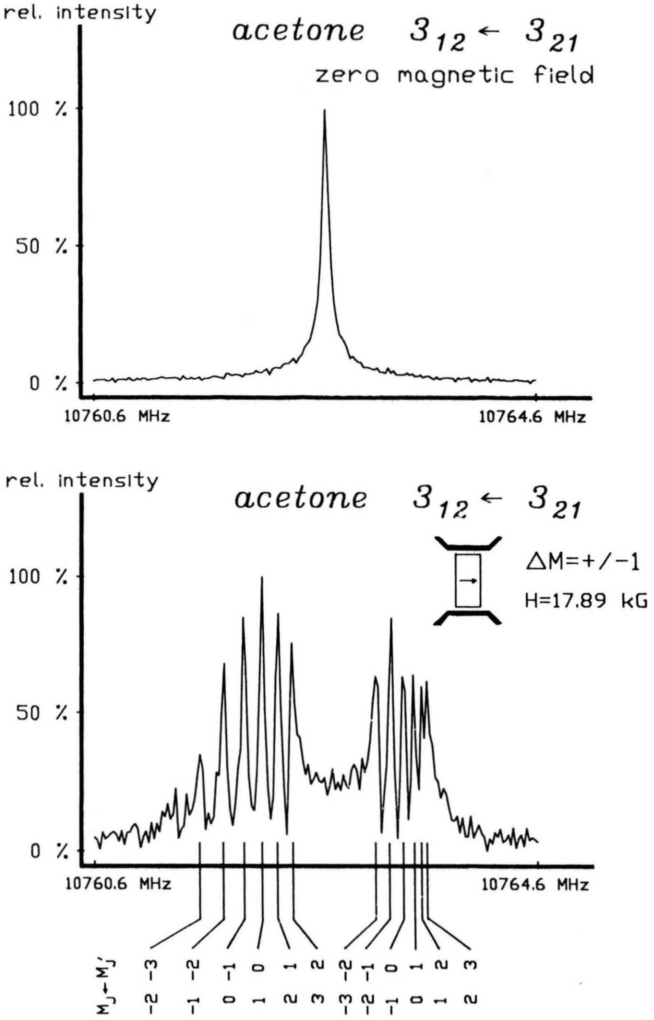

Fig. 3. Fourier transform amplitude spectra corresponding to the transient emission signals shown in Figure 2. The insert shows the orientation of the cross section of the rectangular waveguide absorption cell within the gap of the magnet. The magnetic field, pointing from the upper pole to the lower pole, determines the axis of quantization. With the electric vector of the microwave field perpendicular to the broad face of the waveguide, i.e. perpendicular to the magnetic field, its torque on the molecule changes the angular momentum in the direction of the field. Quantum mechanics leads to the $|\Delta M| = 1$ selection rule. The *M*-quantum numbers of the upper and lower states are given below.

Table 1. Selected zero field and high frequencies determined by direct fits to the recorded transient emission signals [12]. Their absolute uncertainties are largely determined by noise. They are about 4 kHz for the Zeeman satellites and smaller than 2 kHz for the zero field frequencies. The standard rigid rotor Zeeman Hamiltonian was used to calculate the Zeeman splittings presented in the last column. For the g-values and susceptibility anisotropies compare Table 2.

Rotational transition Zero field frequency Magn. field strength	$M' \rightarrow M''$	$(\nu-\nu_0)_{\text{exp}}$/ MHz	$(\nu-\nu_0)_{\text{calc}}$/ MHz
A_1A_1-species			
$1_{11} \rightarrow 0_{00}$ 15996.335 MHz 17865 G	$0 \rightarrow 0$	−0.137	−0.136
$2_{21} \rightarrow 2_{12}$ 15827.741 MHz 15867 G	$-2 \rightarrow -2$	−0.367	−0.370
$3_{21} \rightarrow 3_{12}$ 10762.709 MHz 17891 G	$-3 \rightarrow -2$	−1.128	−1.130
	$-2 \rightarrow -1$	−0.927	−0.928
	$-1 \rightarrow 0$	−0.747	−0.746
	$0 \rightarrow 1$	−0.588	−0.587
	$1 \rightarrow 2$	−0.448	−0.448
	$2 \rightarrow 3$	−0.330	−0.330
	$-2 \rightarrow -3$	0.461	0.462
	$-1 \rightarrow -2$	0.588	0.591
	$0 \rightarrow -1$	0.698	0.698
	$1 \rightarrow 0$	0.783	0.783
	$2 \rightarrow 1$	0.851	0.848
	$3 \rightarrow 2$	0.893	0.892
$3_{21} \rightarrow 3_{12}$ 10762.709 MHz 19680 G	$-3 \rightarrow -2$	−1.263	−1.256
	$-2 \rightarrow -1$	−1.023	−1.025
	$-1 \rightarrow 0$	−0.818	−0.819
	$0 \rightarrow 1$	−0.638	−0.639
	$1 \rightarrow 2$	−0.485	−0.485
	$2 \rightarrow 3$	−0.356	−0.356
	$-2 \rightarrow -3$	+0.515	+0.515
	$-1 \rightarrow -2$	+0.656	+0.657
	$0 \rightarrow -1$	+0.773	+0.773
	$+1 \rightarrow 0$	+0.865	+0.864
$4_{40} \rightarrow 4_{31}$ 16689.830 MHz 15687 G	$+4 \rightarrow +4$	−0.281	−0.282
$5_{32} \rightarrow 5_{23}$ 16943.540 MHz 13137 G	$-4 \rightarrow -4$	−0.347	−0.350
	$+5 \rightarrow +5$	+0.379	+0.380
EE-species			
$1_{11} \rightarrow 0_{00}$ 15074.077 MHz 17864 G	$0 \rightarrow -0$	−0.136	−0.136
$2_{21} \rightarrow 2_{12}$ 15750.854 MHz 17866 G	$-2 \rightarrow -2$	−0.421	−0.418
	$-1 \rightarrow -1$	−0.176	−0.183
$4_{40} \rightarrow 4_{31}$ 16912.377 MHz 17865 G	$-3 \rightarrow -3$	+0.356	+0.361
	$+4 \rightarrow +4$	−0.302	−0.304
$5_{32} \rightarrow 5_{23}$ 16937.686 MHz 19675 G	$-5 \rightarrow -5$	+0.717	−0.715
	$-4 \rightarrow -4$	−0.534	−0.538
$1_{11} \rightarrow 0_{00}$ 15074.076 MHz 16024 G	$-1 \rightarrow 0$	−0.303	−0.304
	$+1 \rightarrow 0$	+0.411	+0.413
$4_{40} \rightarrow 4_{31}$ 16912.377 MHz 18155 G	$+2 \rightarrow +1$	+0.469	+0.468
	$+4 \rightarrow +3$	+0.370	+0.373
$2_{11} \rightarrow 2_{02}$ 11272.459 MHz 17891 G	$-2 \rightarrow -1$	−1.135	−1.125
	$-1 \rightarrow 0$	−0.650	−0.649
	$+0 \rightarrow +1$	−0.302	−0.306
	$+1 \rightarrow +2$	−0.088	−0.095
	$-1 \rightarrow -2$	+0.130	+0.121
	$0 \rightarrow -1$	+0.534	+0.535
	$+2 \rightarrow +1$	+0.958	+0.966
$3_{21} \rightarrow 3_{12}$ 10751.662 MHz 19680 G	$-3 \rightarrow -2$	−1.246	−1.255
	$-2 \rightarrow -1$	−1.017	−1.023
	$-1 \rightarrow 0$	−0.814	−0.817
	$0 \rightarrow +1$	−0.637	−0.636
	$+1 \rightarrow +2$	−0.484	−0.482
	$+2 \rightarrow +1$	−0.357	−0.355
	$-2 \rightarrow -3$	+0.512	+0.512
	$-1 \rightarrow -2$	+0.655	+0.655
	$0 \rightarrow -1$	+0.771	+0.772
	$+1 \rightarrow 0$	+0.862	+0.864
	$+2 \rightarrow +1$	+0.927	+0.929
	$+3 \rightarrow +2$	+0.967	+0.967
$3_{30} \rightarrow 3_{21}$ 11257.731 MHz 17891 G	$-1 \rightarrow 0$	+0.765	−0.765
	$+3 \rightarrow +2$	+0.487	+0.487
	$+1 \rightarrow 0$	+0.582	+0.583
	$0 \rightarrow -1$	+0.702	+0.698

Table 2. Molecular g-values and magnetic susceptibility anisotropies in acetone. Using the standard asymmetric top Hamiltonian, they were determined by fitting to the observed frequencies presented in Table 1. As effective rotational constants we have used $A_{AA} = 10185.877$ MHz, $B_{AA} = 8520.026$ MHz and $C_{AA} = 4910.458$ MHz for the A_1A_1-species (no tunneling), and $A_{EE} = 10162.524$. $B_{EE} = 8523.222$ MHz, and $C_{EE} = 4911.552$ MHz for the EE-species (just one top tunneling). Given uncertainties are single standard deviations from the fit. The sign of the g-values follows from the fact that the opposite choice would lead to unacceptably large values for the molecular electric quadrupole moments.

	A_1A_1-species	**EE-species**
g_{aa}	−0.04379 (8)	−0.04372 (6)
g_{bb}	−0.06611 (5)	−0.06595 (4)
g_{cc}	−0.01481 (7)	−0.01494 (6)
$2\xi_{aa} - \xi_{bb} - \xi_{cc}$	$-9.53\,(21)\ 10^{-6}$ erg $\cdot\, G^{-2}$ mole^{-1}	$-9.28\,(19)\ 10^{-6}$ erg $\cdot\, G^{-2}$ mole^{-1}
$2\xi_{bb} - \xi_{cc} - \xi_{aa}$	$+25.57\,(18)\ 10^{-6}$ erg $\cdot\, G^{-2}$ mole^{-1}	$+25.44\,(15)\ 10^{-6}$ erg $\cdot\, G^{-2}$ mole^{-1}

would have corresponded to perturbations in the same order of magnitude (several %) as are found for the absolute frequencies. But our present experimental knowledge tells that in acetone the effect of tunneling is still below the experimental resolution of our spectrometer. We took this as a justification to procede with the evaluation of the Zeeman data as if acetone were a rigid asymmetric top and used the measured g-values, susceptibility anisotropies and rotational constants of the A_1A_1-torsional species to calculate the molecular electric quadrupole moments according to the equation (c.f. Chapt. II.A in [6] and refs. cited therein)

$$\begin{aligned} Q_{aa} &= (e/2)\{\sum Z_n(2a_n^2-b_n^2-c_n^2) \\ &\quad -\langle 0|\sum(2a_e^2-b_e^2-c_e^2)|0\rangle\} \\ &= -[(h\cdot e)/(16\pi^2 m_p)]\,\{(2g_{aa})/A-g_{bb}/B-g_{cc}/C\} \\ &\quad -[(2mc^2)/(eN)]\,\{2\xi_{aa}-\xi_{bb}-\xi_{cc}\} \qquad (1) \end{aligned}$$

(and cyclic permutations).

In (1) e is the absolute value of the electron charge; a_n, b_n, c_n, a_e, b_e, c_e are the principal inertia axes coordinates of the nuclei and electrons, respectively, and the sums run over the indices of the nuclei, n, and of the electrons, e; m is the electron mass, m_p the mass of the proton; c the velocity of light; N Avogadro's number; and h Planck's constant. Our result for the nonvanishing elements of the molecular electric quadrupole moment tensor of acetone is

$$Q_{aa} = 2.77\,(13)\ \text{DÅ},$$
$$Q_{bb} = -4.59\,(10)\ \text{DÅ},$$
$$Q_{cc} = 1.82\,(15)\ \text{DÅ},$$

if the sign of for the g-tensor elements is choosen as presented in Table 2. For the opposite choice of sign one would obtain unreasonably large absolute values:

$$Q_{aa} = 8.02\ \text{DÅ},\ Q_{bb} = -24.36\ \text{DÅ, and } Q_{cc} = 16.34\ \text{DÅ}.$$

This choice of sign could therefore be discarded.

If one supplements our experimental data for the susceptibility anisotropies by the known bulk value

$$\begin{aligned} \xi_{\text{bulk}} &= (\xi_{aa}+\xi_{bb}+\xi_{cc})/3 \\ &= -33.78\,(20)\ 10^{-6}\ \text{erg G}^{-2}\ \text{mole}^{-1}\ [14], \end{aligned}$$

(uncertainty assumed), the individual components of the susceptibility tensor follow as

$$\xi_{aa} = -36.96\,(21)\ 10^{-6}\ \text{erg G}^{-2}\ \text{mole}^{-1},$$
$$\xi_{bb} = -25.26\,(21)\ 10^{-6}\ \text{erg G}^{-2}\ \text{mole}^{-1},$$
$$\xi_{cc} = -39.13\,(21)\ 10^{-6}\ \text{erg G}^{-2}\ \text{mole}^{-1}.$$

For comparison we present our predicted values:

$$\xi_{aa} = -35.4\,(30),\quad \xi_{bb} = -29.7\,(30),\quad \text{and}$$
$$\xi_{cc} = -39.6\,(30),$$

all in units of 10^{-6} erg G^{-2} mole^{-1}.

Except for the ξ_{bb}-value, which falls slightly out of the predicted uncertainty limits, the other two susceptibilities are found well within their predicted ranges. In this context we find it interesting to note that the out-of plane minus average in-plane susceptibility or $2\xi_{cc}-\xi_{aa}-\xi_{bb}$ is predicted with very reasonable accuracy within a newer additivity scheme devised by J. Spieckermann from our group about two years ago. As increments for the susceptibility tensor he uses tensors ascribed to larger molecular subunits. In our case his subunits CH_3- and $\rangle C{=}O_{(\text{ketones})}$ apply with $2\xi_{cc}-\xi_{aa}-\xi_{bb}$ values of $+2.33$ and -20.57 10^{-6} erg G^{-2} mole^{-1}, respectively. This would lead to a predicted value of -15.91 units for $2\xi_{cc}-\xi_{aa}-\xi_{bb}$ as compared to the experimental value of -16.15 (24) units, i.e. to a prediction within the experimental uncertainties.

Summary

Within the present investigation we could determine the molecular g-tensor and, if supplemented by the bulk susceptibility, the molecular magnetic susceptibility tensor of acetone in its vibronic ground state.

Initially unexpected to us, we found that in the Zeeman patterns the presence of methyl top tunneling is not reflected in measurable deviations from rigid rotor behaviour, at least not in the low-J transitions studied here. (We had expected that, after a rigid rotor optimization of the g-values and susceptibilities, one would be left with mismatches on the order of 10 to 30 kHz).

The experimental susceptibilities were found roughly within the ranges predicted from additivity rules, in which the molecular susceptibility tensor is composed from atomic building blocks. Standard hybridizations are accounted for in the scheme (for instance sp-, sp^2-, and sp^3-carbon atoms are distinguished). But for instance corrections for electronegativity differences between neighbouring atoms are not considered in order to keep the scheme simple. We think that the fair success of the prediction rends some credit to such additivity schemes for use in quick estimates of susceptibility tensors of molecules not yet measured.

Finally the molecular electric quadrupole moment tensor could be determined with reasonable accuracy, and it is hoped that its elements will be of help for the prediction of the equilibrium configuration of van der Waals molecules involving acetone as one of their subunits.

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