On the Validity of Additivity Rules for the Molecular Magnetizability Tensor and the Molecular *g*-Tensor in van der Waals Complexes. A Rotational Zeeman Effect Study of 1,1-Dideutero-Cyclopropane

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Dedicated to Prof. Dr. Helmut Dreizler, who contributed so much to the development of microwave Fourier transform spectroscopy, on occasion of his 65th birthday

The molecular g-tensor and the magnetic susceptibility anisotropy of cyclopropane were determined by a microwave Fourier transform study of the rotational Zeeman effect of its 1,1-dideuterated isotopomer. The results $g_\perp = 0.02675(23)$, $g_\parallel = 0.06998(23)$, and $\xi_\perp - \xi_\parallel = 8.80(31) \cdot 10^{-6}$ erg G^{-2} mol^{-2} are in agreement with values determined indirectly from van der Waals complexes. This finding provides experimental evidence that in van der Waals molecules additivity rules might hold to a high degree of approximation for both types of tensors. Rotational Zeeman effect studies of van der Waals complexes may thus provide valuable extra information on their structures.

Introduction

Additivity rules for molecular tensors, if valid to a sufficiently high degree of approximation, may yield valuable additional information on the average conformation of weakly bound van der Waals complexes. In molecules which contain one or more nuclei with a nonzero nuclear electric quadrupole moment, the nuclear quadrupole coupling tensors have this property. Their insensitivity with respect to dimer formation is plausible, since nuclear quadrupole coupling reflects the torque on the quadrupole nucleus, which is caused by the intramolecular electric field gradient [1]. The latter originates mainly from the electron density in the immediate vicinity of the quadrupole nucleus deep within the molecule and thus remains largely unchanged upon van der Waals complexation.

Aldrich, Kukolich, Campbell, and Read [2] have suggested, that within a van der Waals complex also the molecular magnetizability tensors* (ξ-tensors) as well as the g-tensors of the constituents should be largely insensitive to the formation of the van der Waals bond and, based on this assumption, have used their experimental data for the ξ- and g-tensors of the $C_3H_6 \cdots HCl$ and $C_3H_6 \cdots HCN$ van der Waals complexes for an elegant indirect determination of the elements of the corresponding tensors in the nonpolar cyclopropane subunit.

To cheque their basic assumption we have used the sample of 1,1-dideutero-cyclopropane, which was left over from our previous Stark-effect study [3], for a direct determination of its g- and ξ-tensors by a rotational Zeeman effect study. (For the theoretical and experimental background of rotational Zeeman spectroscopy we refer to [4].) In 1,1-dideutero-cyclopropane the slight imbalance in the vibrational ground state average structures of the CD_2 and CH_2 subunits gives the molecule a small dipole moment parallel to its axis of least moment of inertia and thus makes it accessible to a direct microwave spectroscopic investigation.

Experimental

Our waveguide microwave Fourier transform spectrometer and the 2.5 m electromagnet have been previously described [5]. In-band waveguide absorption cells were used throughout in the present study. A 20 Watt travelling wave tube amplifier was used to amplify the microwave pulses for sufficient polarization of the low-dipole sample ($\mu_a = 0.0115(10)$ D [3]).

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* Here "magnetizability" is used synonymously to "magnetic susceptibility", which was used in our previous publications.

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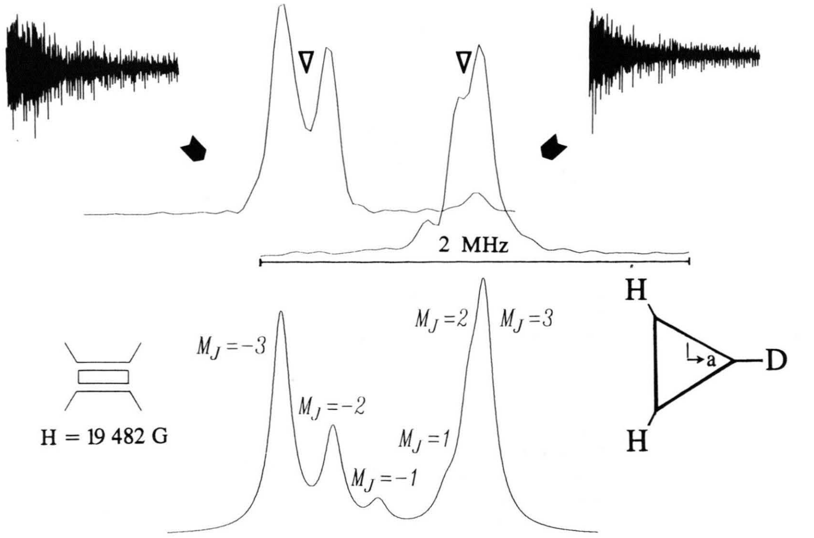

Fig. 1. $\Delta M=0$ Zeemnan multiplet of the $3_{21} \rightarrow 3_{22}$ rotational transition at 11 718.411 MHz (zero-field intensity weighted center frequency of the D-hfs-multiplet). The Zeeman-multiplet was observed under $\Delta M_J=0$; $\Delta M_I=0$ selection rule in a field of 19 482 Gauss. The upper traces show Fourier transform power spectra, calculated from the transient emission signals (upper left and right). The triangles mark the frequencies at which the sample was polarized. Pulses from a 20 W travelling wave amplifier were used to polarize the sample. The lower trace shows a simulation of the Zeeman pattern such as it would be observed in a Stark-effect modulated microwave absorption spectrometer, if sufficient modulation were possible.

Even so, the duration of the pulses had to be extended to the maximum pulse length obtainable with our present spectrometer, and only transitions within a comparatively narrow frequency band of only few hundred kHz around the carrier frequency in the pulse could be reached (compare Figure 1). With a pulse duration of 2.7 μs the signal strengths are extremely sensitive to the frequency offset with respect to the carrier frequency in the pulse. Thus the multiplet presented in Fig. 1 is a composite of two experiments, one with the carrier frequency close to the $M_J=+2$ satellite and one with the carrier frequency between the $M_J=-2$ and $M_J=-3$ satellites. The sample pressure was close to 10 mTorr and the temperature close to $-50\,^{\circ}\mathrm{C}$. From each transient emission 1 K data points were taken at sampling intervals of 10 ns, and the signals from $32 \cdot 10^6$ subsequent transient emissions were averaged for noise reduction.

Analysis

Deuteration not only provides for the small effective electric dipole moment, but also complicates the Zeeman multiplet patterns in so far as it leads to an additional triplet splitting of each M_J-satellite due to deuterium nuclear quadrupole coupling. These triplets could not be resolved. However their patterns could be predicted with fair accuracy. Since the strong magnetic field very effectively uncouples deuterium spin precession and end over end rotation of the molecule, (III.22) in [4] was used for this prediction. For the numerical calculation we have assumed cylindrical symmetry of the deuterium quadrupole coupling tensor around the C–D-bound and a value of 200 kHz for its tensor element in bond direction. With these assumptions the calculated deuterium hfs-satellites typically fall into a frequency range of ± 40 kHz around the center frequency of the corresponding M_J-satellite. Their intensities follow from the deuterium and proton spin weights and leave the intensity weighted mean frequency of each triplet unchanged at the position where the M_J-satellite would be observed if there were no quadrupole coupling. For the analysis of the observed M_J-patterns we have therefore neglected D-hfs completely. Actually the decay-fit routine [6] used to fit the frequencies to the observed transient emission signals failed to fit the individual triplet components within M_J-satellite but succeeded to optimize the central frequencies of sufficiently isolated M_J-satellites with no problem. Only such sufficiently well resolved M_J-satellites (some are presented in Table 1) were used to fit the g-tensor elements $g_\perp$ and $g_\parallel$ and the magnetizability anisotropy $\xi_\perp - \xi_\parallel$ of cyclopropane, C_3H_6. The indices $\perp$ and $\parallel$ indicate the axes perpendicular and parallel to the $\hat{C}_3$ symmetry axis of the undeuterated parent molecule.

For the analysis of the Zeeman splittings we have used the following energy expression for the shifts of the M_J-sublevels upon application of the magnetic

Table 1. Selected Zeeman splittings observed for 1,1-dideutero cyclopropane. Only such transitions are presented here whose frequencies were essentially unperturbed by neighbouring M_J-satellites (compare the text). The Zeeman shifts $\Delta\nu$ are given with respect to the intensity weighted mean frequency of the zero field deuterium hfs multiplet. (The D-hfs structure could not be resolved in the present investigation.)

Transition	Magn. field [Gauss]	$M_{\text{upper}} \to M_{\text{lower}}$	Rel. int. %	$\Delta\nu_{\text{exp}}$ [kHz]	$\Delta\nu_{\text{calc}}$ [kHz]
$1_{01} \to 0_{00}$	17 865	$1 \to 0$	50	−560	−558.0
		$-1 \to 0$	50	609	604.9
	15 687	$1 \to 0$	50	−488	−492.4
		$-1 \to 0$	50	526	528.6
$3_{21} \to 3_{22}$	13 126	$-3 \to -3$	32.14	−347	−342.8
		$3 \to 3$	32.14	280	281.6
	19 482	$-3 \to -3$	32.14	−528	−530.8
		$3 \to 3$	32.14	397	396.0

Table 2. Comparison of the g-tensor elements and the anisotropy of the magnetizability tensor of cyclopropane, C_3H_6, as determined indirectly from the corresponding tensor elements in its van der Waals complexes with HCl and HCN (Aldrich et al. [2]) and directly, from the study of the Zeeman-splittings observed for 1,1-dideutero cyclopropane (present investigation). Our uncertainties represent single standard deviations of the fit.

	$g_\perp = g_{aa,\mathrm{H}} = g_{bb,\mathrm{H}}$	$g_\parallel = g_{cc,\mathrm{H}}$	$(\xi_\perp - \xi_\parallel)$ erg $\mathrm{G}^{-2}\,\mathrm{mol}^{-1}$
Aldrich et al.	0.025(1)	0.067(1)	$9(1) \cdot 10^{-6}$
This work	0.02675(23)	0.06998(23)	$8.8(3) \cdot 10^{-6}$

field H_Z:

$$\Delta W = -\mu_N \cdot H_Z \cdot \frac{M}{J(J+1)} \cdot \left[g_\perp \left(\frac{A_\mathrm{D}}{A_\mathrm{H}} \langle J_a^2 \rangle + \frac{B_\mathrm{D}}{B_\mathrm{H}} \langle J_b^2 \rangle \right) + g_\parallel \frac{C_\mathrm{D}}{C_\mathrm{H}} \langle J_c^2 \rangle \right] - H_Z^2 \frac{(3M^2 - J(J+1)}{3(2J-1)(2J+3)J(J+1)} \cdot (\xi_\perp - \xi_\parallel) \cdot [J(J+1) - 3\langle J_c^2 \rangle]\,. \tag{1}$$

It derives from (III.13) in [4] if the g- and ξ-tensor elements of the deuterated species, $g_{aa}, g_{bb}, \ldots$, are related to those of the undeuterated parent species as (compare (II.6) in [4]):

$$g_{aa} = \frac{A_\mathrm{D}}{A_\mathrm{H}} \cdot g_\perp, \quad g_{bb} = \frac{B_\mathrm{D}}{B_\mathrm{H}} \cdot g_\perp, \quad g_{cc} = \frac{C_\mathrm{D}}{C_\mathrm{H}} \cdot g_\parallel,$$
$$\xi_{aa} = \xi_\perp, \qquad \xi_{bb} = \xi_\perp, \qquad \xi_{cc} = \xi_\parallel\,. \tag{2}$$

For this transformation of the g-tensor elements we have used the following values for the rotational constants of the undeuterated species [7] (index: H) and of the deuterated species [3] (index: D), respectively (all in MHz units):

$$A_\mathrm{H} = 20\,093.3348(28), \quad B_\mathrm{H} = 20\,093.3348(28), \quad C_\mathrm{H} = 12\,555.7498(18),$$
$$A_\mathrm{D} = 18\,835.8616(60), \quad B_\mathrm{D} = 16\,370.2795(20), \quad C_\mathrm{D} = 11\,409.2744(20).$$

In Table 2 we compare the results of our direct determination of the g- and ξ-tensor elements with those deduced by the Urbana group from their measured tensor elements of the van der Waals dimers. Obviously the agreement is quite good, especially for the susceptibility anisotropy, and thus rends credit to their assumption of additivity for the g- and ξ-tensors.

Since an experimental value for the gas phase bulk magnetizability is available from the work of Barter et al. [8],

$$(\xi_{aa} + \xi_{bb} + \xi_{cc})/3 = -39.2(8) \cdot 10^{-6}\,\mathrm{erg\,G^{-2}\,mol^{-1}},$$

also the individual components of the magnetic susceptibility tensor can be given as

$$\xi_{aa} = \xi_{bb} = \xi_\perp = -36.3(8) \cdot 10^{-6}\,\mathrm{erg\,G^{-2}\,mol^{-1}},$$

and

$$\xi_{cc} = \xi_\parallel = -45.1(9) \cdot 10^{-6}\,\mathrm{erg\,G^{-2}\,mol^{-1}},$$

values, which might be also of interest for a comparison with the results of ab initio calculations.

Discussion

At first sight and in view of the changes in the electric dipole moments which have been observed upon dimer formation, it may come as a surprise that additivity rules should hold for the magnetizability tensors. But one should recall: the magnetizability tensor, ξ, basically depends on the second moments of the electronic charge distribution (see (I.4) in [4] and the approximative treatment of the so called "paramagnetic contribution" presented in Chapt. (8-8) of [1]). As compared to the electric dipole moment, these second moments are much less sensitive with respect to the shifts within the electronic cloud, which occur upon formation of the van der Waals bond. For instance, the second electronic moment along the *a*-axis, $\langle | \sum a_j^2 | \rangle$, is left completely unchanged, if electron density is moved from a position $-a$ to a position $+a$, a shift which may result in a sizable change in the *a*-component of the electric dipole moment. (From this point of view the molecular magnetizability tensors of C_3H_6, HCl, and HCN may "by accident" change comparatively little upon complexation, since in the van der Waals complexes $C_3H_6 \cdots HCl$ and $C_3H_6 \cdots HCN$ the van der Waals bond is along a principal inertia axis of the molecular subunits (and of the complex as well).) On the other hand one should also recall that it has been found to be possible to predict the magnetizability tensors of molecules whose bonding situation is reasonably well described by localized bonds, typically within better than 10% from a list of atom magnetizability tensors (say for sp^3-hybridized carbon, sp^2-hybridized carbon etc.; cf. Chapt. II.C in [4]). It therefore appears not unreasonable to expect that additivity should hold to an even much higher degree of approximation for the weakly bound van der Waals complexes.

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