

Study of the hyperfine coupling constants of the molecules NH_2 , NHD and ND_2

K. Funken, B. Engels, S.D. Peyerimhoff

Lehrstuhl für Theoretische Chemie, Universität Bonn, Wegelerstrasse 12, D-5300 Bonn 1, Federal Republic of Germany

and

F. Grein

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2

Received 4 June 1990

In the present paper we calculate the magnetic hyperfine coupling constants (hfcc) a_{iso} and A_{ij} of the ground states of the isotopes NH_2 , NHD and ND_2 using truncated MR-CI methods. Differences from other theoretical methods and shortcomings of the truncated CI approach in calculating a_{iso} are studied. Polarization effects which determine a_{iso} , as well as a simple model to describe the dipolar hfcc's, are discussed. All results are in excellent agreement with experimental data. It is shown that ab initio methods are able to obtain reliable values for off-diagonal values of A_{ij} which are difficult to measure experimentally.

1. Introduction

The amidogen radical, NH_2 , probably represents the most studied triatomic radical at the present time, both by conventional and laser spectroscopic methods. In a series of papers [1–4] Cook, Curl, Hills and coworkers used microwave optical double resonance (MODR) techniques to measure various molecular constants such as rotational constants, centrifugal distortion constants and spin-rotational constants. Also the hyperfine coupling constants (hfcc) composed of the isotropic part a_{iso} and the tensorial anisotropic part A_{ij} were studied for the ground state X^2B_1 and the excited state A^2A_1 . The anisotropic part was interpreted in terms of expectation values for the wavefunction giving a composition of 2% 2s and 90% 2p nitrogen character for the molecular orbital describing the unpaired electron. Because information about the spin-polarization mechanism cannot be derived from experimental data the isotropic part for X^2B_1 , which is determined solely by spin-polarization effects, could not be interpreted in

the same manner. Measurements for the ground state of the two isotopes NHD and ND_2 were performed by the same group [2,4].

The hfcc's of NH_2 are also the subject of several theoretical studies [5–10], whereby the most recent ones are by Sekino and Bartlett [8] and Pöhlchen et al. [9]. The former, who calculated the isotropic part only, used coupled cluster (CC) methods and Møller–Plesset many-body perturbation theory up to fourth order (MBPT4) in connection with basis sets of double-zeta plus polarization quality. This study which discusses differences between the various methods employed finds an agreement with experimental results better than 10%. Similar agreement with experimental data was obtained by Pöhlchen et al. [9] using the CEPA approach in combination with larger basis sets (11s8p3d/10s1p). Their study included calculations of the dipolar part, too.

None of the studies mentioned above investigated the spin-polarization mechanism. Furthermore, the full anisotropic tensor which is necessary to obtain the hfcc of NHD and ND_2 is only given by Brown and Williams [4] who used the UHF method in connection with minimal basis sets. But as expected from

these deficiencies in the method, the deviations from experimental data are substantial.

In the present paper we calculate the hfcc's a_{iso} and A_{ij} of the ground states of all three isotopes NH_2 , NHD and ND_2 using the MRD-CI program package [11]. Differences from other theoretical methods and shortcomings of the truncated CI approach in calculating a_{iso} are studied. Furthermore, polarization effects which determine a_{iso} as well as a simple model to describe the dipolar hfcc are discussed.

2. Theoretical background

The isotropic and anisotropic hfcc's obtained from gas-phase spectra are a direct measure of the net unpaired electron-spin density at the nucleus and the spatial distribution of the electron-spin density, respectively. The former represents a scalar and is defined for a nucleus c as

$$a_{iso}^c = \frac{8}{3}\pi g_N g \beta_N \beta_e \frac{1}{S} \langle \Psi | \sum_{k=1}^n \delta(r_{ck}) s_{zk} | \Psi \rangle,$$

where β_N , g_N are the nuclear magneton and nuclear g factor, respectively. The term g is the g value for the electrons in the free radical, while β_e is the Bohr magneton. In the present work g was set to the value of the free electron g_e . The anisotropic part represents a tensor. Its Cartesian components are defined in a molecule-fixed coordinate system as

$$A_{ij}^c = g_N g_a \beta_N \beta_e \frac{1}{S} \times \langle \Psi | \sum_{k=1}^n \left(\frac{3ij - r^2 \delta_{ij}}{r^5} \right) 2s_{zk} | \Psi \rangle,$$

with $i, j = x, y, z$; ck indicates that A_{ij} is formulated with respect to the center c .

To relate the anisotropic part to experimental data, it has to be taken into account that the relationship between a molecule-fixed and a space-fixed axis system is determined by the much stronger rotational interaction rather than by the hyperfine interaction [12]. For a near-prolate asymmetric rotor ($I_a < I_b < I_c$, I_n denotes the inertial tensor components within its principal axis system a, b, c , see fig. 1) such as NH_2 , the rotational problem cannot be solved in closed form. One way to obtain the rotational spec-

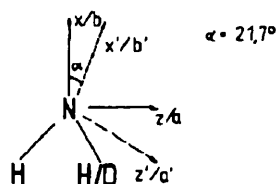


Fig. 1. Different principal axes of the inertial tensor I for the molecules NH_2 (solid lines) and NHD (dotted lines). The principal axis y/c comes out of the molecular plane and is identical in both molecules. The I' identification ($x \leftrightarrow b, y \leftrightarrow c, z \leftrightarrow a$) [13] is indicated at the axes.

tra is to expand the problem into a prolate symmetric-top rotor basis, $|NKM\rangle$, with N representing the rotational moment and M being the projection of N onto the space-fixed Z axis. The letter K is the component of N along the axis within the molecule-fixed axis system which lies along the axis a of the inertial tensor. For a symmetric top molecule, K also is a constant of motion. The rotational energy levels are obtained by diagonalizing the given matrix problem.

It can be shown that for a near-prolate asymmetric rotor, the off-diagonal elements of the matrix, representing the differences between a symmetric and asymmetric rotor, are minimized if the I' identification ($x \leftrightarrow b, y \leftrightarrow c, z \leftrightarrow a$) between space-fixed and molecule-fixed axis system is chosen [13]. Other possible relationships could also be taken but the I' is the most convenient.

Other perturbations to the rotational structure of the spectra such as spin-rotation interaction or hyperfine interactions, for example, are taken into account by including the appropriate matrix elements in the rotational matrix. Those matrix elements appear both as diagonal and as off-diagonal elements. The spectroscopic parameters describing the various interactions are obtained by diagonalizing the combined matrix. A more detailed discussion of the problem can be found in refs. [14,15]. Keeping the I' identification also for the anisotropic part A_{ij} is essential because the off-diagonal components in A_{ij} for the hydrogen centers, A_{ij}^H , only contribute to matrix elements off-diagonal in rotational quantum number K ($\Delta K = \pm 1$), and the resulting second-order perturbation effects are too small to be detectable [15]. Normally the A_{ij} are constrained to be zero.

Therefore, from standard experiments not all elements of A_{ij}^H can be determined but only those along the principal axis of the inertial tensor I . Hence a direct comparison between theoretical and experimental results in which A_{ij}^H is given in its own principal axis system is normally not possible.

The off-diagonal element A_{ij}^H of NH_2 can be determined from experimental data of the NHD molecule because it possesses different principal axes of the inertial tensor I' . Knowing the angle between the two principal axis systems I and I' , one can calculate A_{ij}^H of NH_2 from the diagonal elements of the NHD molecule. This was done by Steimle et al. [2].

From ab initio studies, which calculate A_{ij} within the rigid molecule, all elements of A_{ij} are obtained directly. This it is possible to calculate the anisotropic hfcc's of NHD from the NH_2 results simply by rotating the A_{ij} tensor into the new principal inertial axis system. For the deuterium center also the g_N value has to be changed. All this is possible within the Born–Oppenheimer approximation (BO) because in this approximation there is no difference between the electronic structures of NH_2 and NHD. Beyond the Born–Oppenheimer approximation, further effects arise from the influence of the nuclear motion, but it was found that for the two lowest vibrational states of NH_2 [10] the hfcc's depend only very slightly on the vibrational states. Since for the NHD molecule the $\nu=0$ level is even lower than in NH_2 , vibrational effects were neglected in the present paper. The agreement between theoretical and experimental results (see below) supports this assumption.

It is known [16] that from a theoretical point of view $a_{i\infty}$ is much more difficult to calculate than A_{ij} , although the problems just discussed for the anisotropic part do not exist because $a_{i\infty}$ represents a scalar. The difficulties in the $a_{i\infty}$ calculations arise since only those orbitals contribute which possess a non-vanishing value at the position of the nucleus in question and a net spin density. For X^2B_1 of NH_2 the Hartree–Fock determinant is given by $1a_1^2 2a_2^2 3a_3^2 1b_2^2 1b_1^2$. Because the singly occupied $1b_1$, which represents a nearly pure nitrogen p_y orbital, possesses a node in the molecular plane, a restricted Hartree–Fock calculation (RHF) gives $a_{i\infty}=0$ for all centers so that the value of $a_{i\infty}$ is determined solely by spin-polarization effects. The A_{ij} values, on the

other hand, are expected to be dominated by the RHF value because here $1b_1$ can contribute.

3. Method of calculation

The basis sets employed are identical to those used for the NH molecule [17]. They are summarized in table 1. Although basis set effects on A_{ij} were found to be stronger than in the NH molecule, no f functions were added. Their influence is expected to be about 1 MHz. An extensive discussion of basis set effects on $a_{i\infty}$ and A_{ij} can be found elsewhere [10]. Most of the CI calculations were performed by using molecular orbitals (MO) acquired from a RHF calculation of the ground state. To obtain a faster convergence of the CI expansions, natural orbitals (NO) were also employed. The calculations were performed at the equilibrium geometry with $R_{\text{NH}}=1.935$ au, $\theta=103.3$ [19].

4. Results and discussion

Because $a_{i\infty}$ is determined by spin polarization effects, a strong dependence on the quality of the CI wavefunction employed is expected. The dependence for the X^2B_1 state in NH_2 is shown in fig. 2. The calculations are carried out in the standard manner whereby the MRD-CI truncation is made on the basis of the energy selection threshold T [11]. The effect of higher excitations can be seen from a comparison between results of a SD-CI (1 reference configuration) and those obtained from a multi-reference CI (23 reference configurations for the NO calculation, 10 reference configurations for MO cal-

Table 1
Technical details

AO basis sets employed in the present work:	
nitrogen	(13s8p) contracted to – [8s5p] according to refs. [17,18] plus 2d (1.9/0.5)
hydrogen	(8s) contracted to – [5s] according to refs. [17,18] plus 2p (1.4/0.25)
Basis used for CI calculations:	
MO basis:	from RHF-SCF calculation of X^2B_1 .
NO basis:	from 1M1R MRD-CI calculation with $T=10.0$ μ hartree employing MOs

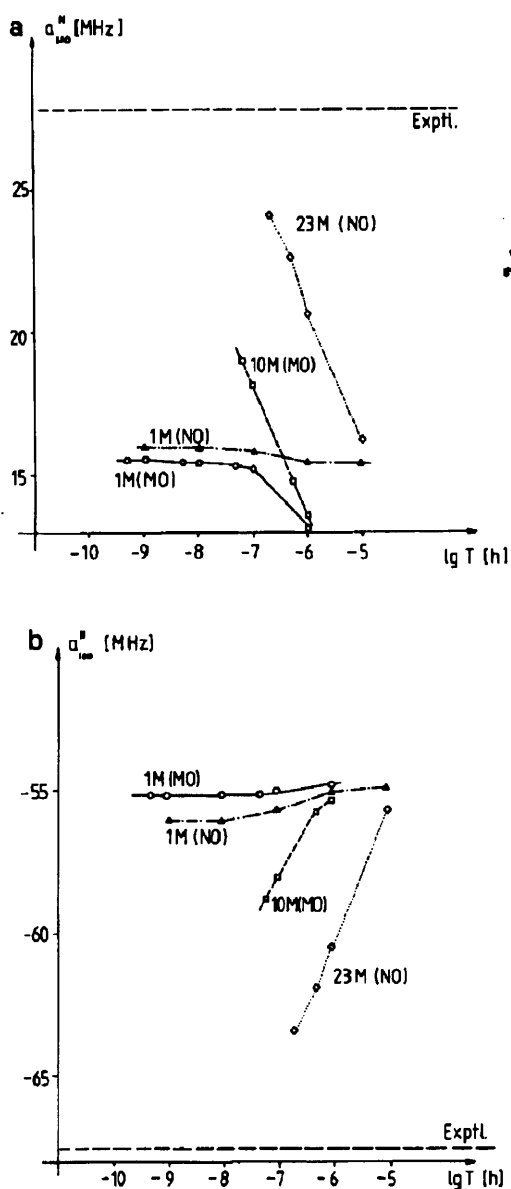


Fig. 2. (a) Calculated values for a_{iso}^N in various treatments. The number of reference configurations (M) is always indicated as well as the basis (molecular orbital (MO) or natural orbital (NO)). The values are given as a function of the threshold T for configuration selection (see text). (b) Calculated values for a_{iso}^H in various treatments. The notation is identical to (a).

calculation). The reference configurations were selected on the basis of their contribution to the total wavefunction. The total space consisted of 19015 state functions in the SD-CI treatment and 515792 in MRD-CI calculations employing 10 reference

configurations (906999 for the 23 M calculation using NOs). Hence at a configuration-selection threshold of $T=6 \times 10^{-8}$ hartree, 17568 state functions, i.e. about 3.4% of the total space, were included (17534 or 1.9% if NOs were employed).

The influence of higher excitations is considerable and an extrapolation to the full MRD-CI space or an estimate of the full CI space, which is generally possible for the energy, is not yet feasible for the a_{iso} values based on the energy-selected configurational subspace below 18000 configurations. The calculated absolute values of a_{iso} are too small in comparison to experimental results. It is seen that an improvement of the CI calculations by incorporating more of the weakly interacting configurations which were previously neglected narrows the gap between theory and experiment. It is also important to see that even though the SD-CI treatment appears to converge, its value is about 10 MHz in error.

In table 2 results of the present study are compared with hfcc's obtained by other theoretical methods. The high accuracy in the description of correlation effects which is necessary to obtain a reliable value for a_{iso} is easily seen. The dipolar constants, on the other hand, are known [16] to be influenced more by basis set deficiencies than by correlation effects. This explains the deviations found for the results of Brown and Williams [4] who used minimal basis sets only. The whole tensor A_{ij} including the outer-diagonal elements are only given by Brown and Williams [4] and the present work.

In order to understand differences in a_{iso}^H between the MRD-CI, CEPA and CC results, the basis sets employed in the given studies have to be considered. From the study of $X^3\Sigma^-$ of NH [17] it is known that the use of polarization functions lowers the magnitude of the calculated value of a_{iso} at both centers. Furthermore, a_{iso} of a given center is mostly influenced by the basis set located at the center itself. Effects from functions located at different centers are found to be smaller. On this basis, the differences between the MRD-CI and CEPA studies on one side and the CC results on the other are understandable. Sekino and Bartlett [8] used a basis set of double-zeta quality augmented by one polarization function at each center. It is smaller than that used by Pöhlichen et al. [9] (11s6p3d/10s1p) or in the present study (table 1). The deviations in a_{iso}^H between

Table 2

Comparison between hyperfine coupling constants (in MHz) for X^2B_1 of NH_2 obtained by various theoretical methods

		MRD-CI ^{a)}	CEPA ^{b)}	CCSD ^{c)}	SF-CI ^{d)}	UHF ^{e)}	UHF ^{f)}	exp. ^{g)}
nitrogen center	a_{iso}	24.1	24.3	25.2	17.9	42.0	99.0	27.9
	A_{aa}	-42.4	-42.7				-32.0	-43.1
	A_{bb}	-42.9	-44.7				-36.0	-44.6
	A_{cc}	85.3	87.4				70.0	87.7
	A_{ab}	0.0					0.0	0.0
hydrogen center	a_{iso}	-63.4	-58.6	-72.9	-61.3	-101.6	-171.0	-67.2
	A_{aa}	20.1	16.0				30.0	18.6
	A_{bb}	-13.0	-12.5				-5.0	-13.4
	A_{cc}	-7.3	-3.5				-25.0	-5.2
	A_{ab}	55.7					71.0	58.5

^{a)} Present work (NO, 23 mains, $T=2 \times 10^{-7}$). ^{b)} Ref. [9] ^{c)} Ref. [8]. ^{d)} Ref. [7]. ^{e)} Ref. [7]. ^{f)} Ref. [4]. ^{g)} Ref. [3].

our study and the CEPA results are, however, somewhat surprising. A possible explanation is the strong dependence of a_{iso} on higher excitations such as triple or quadruple excitations.

The general conclusion from table 2 is that if correlation effects are taken into account, a close agreement for a_{iso} and A_{ij} is found between the various methods whereby the hydrogen results, however, deviate more from each other than the nitrogen constants. For methods which do not incorporate correlation effects properly, such as UHF, larger errors are found.

The hfcc of a free radical like NH_2 may be interpreted in terms of expectation values for the wavefunction of the unpaired electron [20], thus giving a direct experimental characterization of the MO describing the unpaired electron. For NH_2 , only A_{ij} can be used since the a_{iso} values are solely determined by spin-polarization effects. Information about the spin-polarization mechanism which cannot be extracted from experimental results can be obtained from core calculations [21], i.e. calculations in which together with the $1b_1$ electron only the electrons of one doubly occupied shell are correlated. The results are summarized in table 3. Because core calculations represent a simplification, i.e. do not include correlation effects between doubly occupied shells, only calculations employing MOs (but not NOs) were performed.

The situation is similar to that found for the NH molecule. The value at the nitrogen center, a_{iso}^N , is composed from contributions of $1a_1$, $2a_1$ and $3a_1$.

Table 3

The value for a_{iso} (in MHz) obtained from core calculations for X^2B_1 of NH_2 (MO basis)

Center	Correlated shell ^{a)}				Sum ^{b)}
	$1a_1$	$2a_1$	$3a_1$	$1b_2$	
nitrogen	-51	60	12	0	21
hydrogen	0	-35	7	-22	-50

^{a)} Correlated shell means that only the shell given is correlated together with the $1b_1$ shell, while all other shells are kept doubly occupied.

^{b)} The sum of the single contributions is given to indicate that a_{iso} cannot be completely calculated without including inter-shell correlation effects.

(The $1b_2$ cannot contribute because it possesses a node at the nitrogen center.) The $1a_1$ and $2a_1$ contributions are large and because they possess different signs, a partial cancellation occurs. The $3a_1$ contribution is smaller in magnitude. For the hydrogen centers, the $1a_1$ does not contribute since it represents the nearly undistorted nitrogen $1s$ orbital. The value of a_{iso}^H is determined by contributions from $2a_1$ and $1b_2$ while again the $3a_1$ is less important. The investigation of a_{iso}^H shows clearly that the value cannot be related to a single molecular orbital, i.e. the highest doubly occupied orbital. For a_{iso}^N the situation seems somewhat simpler because partial cancellation of the $1a_1$ and $2a_1$ contributions occurs.

The influence of the multi-reference CI on the value of the dipolar tensor A_{ij} has also been studied [10] but was found to be very small, as expected. A

RHF calculation for A_{ij} which is identical to the computation of the expectation value of A_{ij} for the $1b_1$ orbital gives already 98% of the total value. The calculations support the experimental conclusion that the singly occupied orbital possesses 95% p contribution. A simplified model for a qualitative description of A_{ij} can be made. The relative weight and the signs of the components are reproduced by calculations in which the unpaired electron is localized about 1.2 au above and below the nitrogen center, and further improvement is reached if it is shifted slightly towards the hydrogen centers (by about 0.1 au). For a quantitative description the electron distribution has to be taken into account, i.e. by using the RHF orbital. A similar model was used by Steimle et al. [2] to fit their experimental results. As was shown elsewhere [10], this model is also sufficient to explain the qualitative behavior of A_{ij} over a large range

of varying bond distances or bond angles.

As discussed above, within the BO approximation the NH_2 results can be used to calculate hfcc's of NHD if proper scaling of g_N and appropriate coordinate transformations are performed. The principal axes of the inertial tensor I of NH_2 can be transformed into that of NHD by a rotation of about 21.7° in the ab plane (fig. 1). To compare the A_{ij} of NHD with experimental results which are measured along the principal axis of I , A_{ij} has to be transformed in the same manner. The results are summarized in table 4 where the ND_2 values are also given. The isotropic values are not influenced by this transformation and are given for completeness. For symmetry reasons the A_{cc}^H values are not affected by the rotation so that they are equal in both molecules. The large effect of the rotation for A_{ij}^H is due to the strong differences in A_{aa}^H and A_{bb}^H and the large value of

Table 4
Comparison between theoretical ^{a)} and experimental results ^{b)} for hyperfine coupling constants of NH_2 , NHD and ND_2 (values in MHz)

		Nitrogen		Hydrogen			
		theory	exp.	theory	exp.		
NH_2 molecule	a_{iso}	24.1	27.8	-63.4	-67.6		
	A_{aa}	-42.4	-43.1	20.1	18.6		
	A_{bb}	-42.9	-44.6	-13.0	-13.4		
	A_{cc}	85.3	87.7	-7.3	-5.2		
	A_{ab}	0.0	0.0	55.7	58.5 ^{c)}		
		Nitrogen		Hydrogen		Deuterium	
		theory	exp.	theory	exp.	theory	exp.
NHD molecule	a_{iso}	24.1	27.8	-63.4	-67.6		
	A_{aa}	-42.5	-43.0	-22.3	-25.5	8.2	8.2
	A_{bb}	-42.8	-44.4	29.5	30.5	-7.1	-7.4
	A_{cc}	85.3	87.5	-7.3	-5.2	-1.1	-0.8
	A_{ab}	0.2		51.4		-4.4	
		Nitrogen		Deuterium			
		theory	exp.	theory	exp.		
ND_2 molecule	a_{iso}	24.1	27.8	-9.7	-10.1		
	A_{aa}	-42.4	-43.0	3.1	3.1		
	A_{bb}	-42.9	-44.4	-2.0	-2.1		
	A_{cc}	85.3	87.5	-1.1	-0.9		
	A_{ab}	0.0		8.5			

^{a)} Present work (NO, 23 mains, $T=2 \times 10^{-7}$).

^{b)} Steimle et al. [2], Hills and Cook [3].

^{c)} Obtained indirectly from NHD measurements [2].

A_{ab}^H in NH_2 . Because for the nitrogen center A_{aa}^N is nearly identical to A_{bb}^N and A_{ab}^N is zero, nearly no effect of the rotation is seen for the dipolar tensor of the nitrogen center. For all three molecules a very good agreement is found. This is expected from the agreement of the NH_2 results with experimental values and shows that effects beyond the BO approximation are small.

5. Conclusion

In the present paper we have discussed the hfcc's for the X^2B_1 state of NH_2 . The values were used to calculate hfcc's for the ground state of the isotopes NHD and ND_2 (table 4) by transforming the A_{ij} tensor onto the principal axis system of the inertial tensor I of the given molecule. All results are in very good agreement with experimental data which shows that effects beyond the BO approximations are small. Deviations, which are around 2–3 MHz, can be traced to the strong influence of correlation effects and to small basis set deficiencies for the isotropic and anisotropic parts, respectively. It can clearly be seen that ab initio methods are able to obtain reliable values for off-diagonal elements in A_{ij} , which are difficult to measure by experimental methods.

The spin-polarization mechanism which determines a_{iso} was investigated by core calculations (table 3). By symmetry, only a_1 orbitals can contribute to a_{iso}^N . A partial cancellation of the negative $1a_1$ and the positive $2a_1$ contribution is found whereby both single values are large in comparison to the positive $3a_1$ contribution. The total value of a_{iso}^H is determined from negative $2a_1$ and $1b_2$ contributions. The $3a_1$ contribution is positive but smaller in magnitude. The A_{ij} values, which are nearly independent of correlation effects, can be described by a crude model in which the unpaired electron is localized above and beneath the nitrogen center.

Acknowledgement

The authors wish to thank the Deutsche Forschungsgemeinschaft for financial support given to this work. The services and computer time made

available by the University of Bonn Computer Center are gratefully acknowledged. A NATO grant for international collaboration in research greatly facilitated the interaction between the Universities of Bonn and New Brunswick. A grant of NSERC is also gratefully acknowledged. One of us (BE) would like to thank all members of the Chemistry Department of the University of New Brunswick for their efforts in making his visit a pleasant and fruitful one.

References

- [1] G.W. Hills, J.M. Cook, R.F. Curl Jr. and F.K. Tittel, *J. Chem. Phys.* 65 (1976) 823; J.M. Cook, G.W. Hills and R.F. Curl Jr., *J. Chem. Phys.* 67 (1977) 1450; G.W. Hills, C.R. Brazier, J.M. Brown, J.M. Cook and R.F. Curl Jr., *J. Chem. Phys.* 76 (1982) 240.
- [2] T.C. Steimle, J.M. Brown and R.F. Curl Jr., *J. Chem. Phys.* 73 (1980) 2552.
- [3] G.W. Hills and J.M. Cook, *J. Mol. Spectry.* 94 (1982) 456.
- [4] J.M. Cook and G.W. Hills, *J. Chem. Phys.* 78 (1983) 2144.
- [5] R.D. Brown and G.R. Williams, *Chem. Phys.* 3 (1974) 19.
- [6] W. Meyer, *J. Chem. Phys.* 51 (1969) 5149.
- [7] K. Ohta, H. Nakatsuji, K. Hirao and T. Yonezawa, *J. Chem. Phys.* 73 (1980) 1770.
- [8] H. Sekino and R. Bartlett, *J. Chem. Phys.* 82 (1985) 4225.
- [9] M. Pöhlichen, V. Staemmler and R. Jaquet, *Konferenz für Theoretische Chemie, Ponteresina* (1988).
- [10] K. Funken, *Diplomarbeit Bonn* (1988).
- [11] R.J. Buenker and S.D. Peyerimhoff, *Theoret. Chim. Acta* 12 (1968) 183; 39 (1975) 217.
- [12] W. Gordy and R.L. Cook, *Microwave molecular spectroscopy in technique of organic chemistry*, ed. A. Weissenberger (Wiley-Interscience, New York, 1970); P.R. Bunker, *Molecular symmetry and spectroscopy* (Academic Press, New York, 1979).
- [13] J.K.G. Watson, in: *Vibrational spectra and structure*, Vol. 6, ed. J.R. Durig (Elsevier, Amsterdam, 1977).
- [14] I.C. Bowater, J.M. Brown and A. Carrington, *Proc. Roy. Soc. A* 333 (1973) 265.
- [15] T.J. Sears, *Comput. Phys. Rept.* 2 (1984) 1.
- [16] D. Feller and E.R. Davidson, *J. Chem. Phys.* 80 (1984) 1006.
- [17] B. Engels and S.D. Peyerimhoff, *Mol. Phys.* 67 (1989) 583.
- [18] F.B. van Duyneveldt, *Technical Report RJ945*, IBM Research Laboratory, San Jose, CA, USA.
- [19] P.B. Davis, D.K. Russel and B.A. Thrush, *Proc. Roy. Soc. A* 535 (1977) 299.
- [20] R.F. Curl Jr., *J. Chem. Phys.* 37 (1962) 779.
- [21] B. Engels and S.D. Peyerimhoff, *J. Phys. B* 21 (1988) 3459.