

MOLECULAR-BEAM ELECTRIC-RESONANCE STUDY OF CYANOGEN CHLORIDE (ClCN)

J.M.L.J. REINARTZ, W.L. MEERTS and A. DYMANUS

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

Received 23 April 1979; in final form 25 September 1979

The molecular-beam electric-resonance (MBER) method has been used to determine the hyperfine structure and the electric and magnetic properties of $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ in the ground and first excited bending vibrational state. For the ground state the observed quantities are the electric quadrupole coupling tensor component (eQq_{zz}), and the spin-rotation coupling constant (c_{\perp}) perpendicular to the molecular axis (of ^{35}Cl and ^{14}N); the electric dipole moment (μ_{el}), the molecular g -factor perpendicular to the molecular axis (g_{\perp}), and the anisotropy in the magnetic susceptibility ($\chi_{\parallel} - \chi_{\perp}$). The same constants, except the magnetic properties, have also been determined for the first excited bending vibrational state (01¹0). The l -doubling constants q_0 and μ_{\perp} , perpendicular anisotropy in the electric quadrupole moment tensor ($eQq_{xx} - eQq_{yy}$) and anisotropy of the spin-rotation constants in directions parallel and perpendicular to the molecular axis ($c_{\parallel} - c_{\perp}$) have been obtained for the first bending vibrational state.

1. Introduction

In a series of papers on triatomic linear molecules we have reported accurate studies of electric and magnetic properties and of l -doubling of OCS [1-3] and N_2O [4] both in the ground and in the excited bending vibrational mode. Detailed information on other linear triatomic molecules for the excited bending vibrational states has been reported only for HCN [5, 6]. Cyanogen chloride (ClCN) was chosen for the present investigation for a number of reasons. Contrary to N_2O , where the electric quadrupole effects are small as compared to the l -doubling effects in the (01¹0) state, ClCN exhibits large energy contributions due to the electric quadrupole moment of ^{35}Cl relative to the l -doubling in the lower J -states for (01¹0) vibration. Further, previous investigations concerned triatomic molecules with very small (N_2O) or intermediate (OCS) values for the electric dipole moments, whereas ClCN has a relatively large molecular electric dipole moment.

To our knowledge there are no recent studies on $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ isotopic species in the ground or excited bending state performed. Rough values of hyperfine constants have been reported by White [7] determined from microwave spectroscopy. Rotational constants for several isotopes and a first value for the electric dipole moment obtained with a Stark modulation spectrometer have been reported by Tyler and Sheridan [8]. A study of the Zeeman properties has been performed by Ewing et al. using microwave spectroscopy [9].

This work reports an MBER study of $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ which yielded accurate values for hyperfine constants and electric dipole moments in the $v_2 = 0$ and $v_2 = 1$ states and of magnetic properties in the $v_2 = 0$ and l -doubling properties in the $v_2 = 1$ states. The spectra of the ground vibrational state could be explained within the experimental accuracy of about 100 Hz by the well-known theory for linear molecules in a $^1\Sigma$ electronic state. The theory presented in earlier work [4, 10] was used to calculate the spectra of the $v_2 = 1$ state.

The derived molecular constants such as the molecular quadrupole moment, and the nuclear magnetic shielding factors of ^{35}Cl and ^{14}N in ClCN are given. The last quantities were derived by combining the values obtained for the c -constants with the atom-dipole method calculation of the diamagnetic shielding contributions [11].

2. Theory

The hamiltonian used for the interpretation of the MBER spectra of linear molecules, contains the following terms:

$$H = H_{\text{VR}} + H_{\text{HF}} + H_E + H_B. \quad (1)$$

In this equation the successive contributions to the hamiltonian represent in this order the vibration-rotation interaction (H_{VR}), the hyperfine energy (H_{HF}) and the interaction energy of the molecule in an external electric (H_E) and magnetic (H_B) field, respectively.

The energy matrix has been calculated on the basis $|v_2^l J M_J \pm\rangle$ which is defined as

$$|v_2^l J M_J \pm\rangle = 2^{-1/2} [|v_2 l\rangle |J l M_J\rangle \pm (-1)^J |v_2(-l)\rangle |J(-l) M_J\rangle], \quad (2a)$$

for $l \neq 0$ and

$$|v_2^0 J M_J\rangle = |v_2 0\rangle |J 0 M_J\rangle, \quad (2b)$$

for $l = 0$.

In the symmetrized wavefunctions of eq. (2) $|v_2(\pm l)\rangle$ is shorthand notation for the vibrational wavefunction $|v_1 v_2 v_3\rangle$ and $|J(\pm l) M_J\rangle$ for the rotational wavefunction. The latter function is related to the symmetric top function [12]

$$|J(\pm l) M_J\rangle = [(2J + 1)/8\pi^2]^{1/2} \mathcal{D}_{\pm l M_J}^{(J)}(\alpha\beta\gamma). \quad (3)$$

The quantum numbers v_1, v_2, v_3, J, M_J and l have their well established (standard) meanings. The nonvanishing contributions to the hyperfine energy matrix for a molecule in a $^1\Sigma$ electronic state originate in the interaction of the nuclear tensor \mathbf{Q}_K of nucleus K with the gradient tensor \mathbf{V}_K of the electric field due to other nuclei and electrons at the position of the nucleus, in the interaction of the spin of nucleus $K(I_K)$ with the magnetic field produced by

the molecular rotation \mathbf{J} and in the nuclear spin-spin interaction. The hamiltonian describing these interactions can be written

$$H_{\text{HF}} = \sum_K \mathbf{Q}_K \cdot \mathbf{V}_K + \sum_K I_K \cdot \mathbf{M}_K \cdot \mathbf{J} + \sum_{L>K} I_K \cdot \mathbf{D}_{KL} \cdot I_L, \quad (4)$$

where \mathbf{M}_K and \mathbf{D}_{KL} is the nuclear spin-rotation and spin-spin interaction tensor, respectively. The contributions to the energy due to interactions of the molecule with external electric (\mathbf{E}) and magnetic (\mathbf{B}) fields are deduced from

$$H_E + H_B = -\mu_{\text{el}} \cdot \mathbf{E} - \frac{1}{2} \mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E} - \mathbf{B} \cdot \mathbf{G} \cdot \mathbf{J} - \frac{1}{2} \mathbf{B} \cdot \boldsymbol{\chi} \cdot \mathbf{B} - \sum_K (\mu_K/I_K) I_K \cdot (\mathbf{1} - \boldsymbol{\sigma}_K) \cdot \mathbf{B} - \mu_{\text{el}} \cdot \mathbf{v} \times \mathbf{B}. \quad (5)$$

In this expression the successive terms describe energy contributions due to Stark effect (μ_{el} is the electric dipole moment), the electric polarizability ($\boldsymbol{\alpha}$ is the polarizability tensor), the molecular Zeeman effect (\mathbf{G} is the magnetic rotational tensor), magnetic susceptibility (tensor $\boldsymbol{\chi}$), the nuclear Zeeman effect ($\boldsymbol{\sigma}_K$ is the nuclear shielding tensor and μ_K the magnetic dipole moment of nucleus K) and the translational Stark effect (\mathbf{v} is the molecular velocity in the beam).

Matrix elements have been calculated using spherical tensor operator techniques [12, 13] and the symmetrized wavefunctions of eq. (2) in the coupling scheme

$$I_1 + J = F_1 \quad \text{and} \quad F_1 + I_2 = F.$$

A complete treatment of the calculation of the matrix elements is given in ref. [10] and a survey of those calculations relevant for the present study of ClCN in ref. [4].

3. Experiment

The MBER machine used in the present investigations has been described previously [10, 14]. The transitions observed in the ground vibrational state were $\Delta J = 0, \Delta M_F = 0, J = 1$ in an electric and in a combined electric and magnetic field. The $v_2 = 1$ spectra were $\Delta J = 0$ l -doubling of $J = 2$ and $J = 3$ in zero external field. The electric dipole moment of

the $v_2 = 1$ state has been determined from Stark transitions in the $J = 2$ state.

Special precautions have been taken in working with the corrosive gas in the poisonous quantity necessary for performing MBER spectroscopy. A stainless steel regulator (l'Air Liquide DIRS No. 6) was used to reduce and regulate the pressure.

A configuration built of special valves proof against highly corrosive gases connected to stainless steel tubes served for further flow of the gas to the nozzle source. The molecular beam source has been equipped with a 100 μm nozzle. The optimum signal to noise ratio for the spectral lines was reached at a backing pressure of 0.08 bar (60 Torr) and was typically 15 and 3 using an RC time of 1 s for the transitions in the $v_2 = 0$ and $v_2 = 1$, respectively.

The beam signal was monitored at the parent ion mass peak of $m/e = 61$ (the $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}^+$ -ion).

The effective transition region in the C-field was 20 cm. Under these conditions the full line width at half height was 1.5 kHz and 1.8 kHz for the $v_2 = 0$ and the $v_2 = 1$ transitions, respectively.

4. Results

The transition frequencies expressed in terms of coupling constants have been obtained by diagonalizing the energy matrix.

In the case of $v_2 = 0$ the total energy matrix of $J = 0$ through 3 was calculated and diagonalized. The $v_2 = 1$ energy levels were calculated for each J state separately. However, because of the large quadrupole moment of the Cl-nucleus non-negligible contributions from the interaction of the $\sum_K \mathbf{O}_K \cdot \mathbf{V}_K$ operator off-diagonal in J , had to be taken into account. Simple first order perturbation theory has been applied to include those contributions [15]. A least-squares minimizing procedure followed to determine the coupling constants. The physical constants used in the evaluation of those constants are taken from ref. [16]. Accuracies of constants reported in this paper are given with at least 95% confidence according to the confidence level tables of Fisher and Yates [17].

4.1. Cyanogen chloride in the ground vibrational state

The $\Delta J = 0$, $\Delta M_F = 0$, and ± 1 transitions have been observed in an electric field of 471.44 V/cm. Such a field causes Stark shifts up to 37 MHz for $J = 1$ states and up to 9 MHz for $J = 2$ states. In total 27 transitions originating in the $J = 1$ state were used to determine the molecular constants μ_{e1} , $eQ_{\text{Cl}}q_{\text{C}}^{\text{Cl}}$, $eQ_{\text{N}}q_{\text{C}}^{\text{N}}$, c_{C}^{Cl} , c_{N}^{N} given in table 1. The spin-spin interaction constant $d_T = 0.039$ kHz has been calculated from the geometry of the molecule.

Since only one rotational state has been investigated, it was not possible to separate the Stark effect contributions due to the electric dipole moment from those due to the electric polarizability [18]. To our knowledge no accurate value of $\alpha_{\parallel} - \alpha_{\perp}$ for $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ has been reported in the literature. However, for values of $(\alpha_{\parallel} - \alpha_{\perp})$ smaller than 10^{-29} m³ the effect on the determination of μ_{e1} can be neglected to within its quoted experimental error. The value for μ_{e1} given in table 1 can be regarded as the absolute electric dipole moment.

The Stark-Zeeman spectra have been obtained for an electric field of 471.47 V/cm and a parallel magnetic field of about 0.87 T. Twenty-one $\Delta M_F = 0$ transitions were measured. The magnetic field strength was calibrated using the $\Delta J = 0$, $\Delta M = \pm 1$ transitions of the $J = 1$ state in OCS [1]. Six magnetic constants determined the spectrum in the presence of a magnetic field g_{\perp} , $g_{I_{\text{Cl}}}(1 - \sigma_{\text{Cl}}^{\text{Cl}})$, $g_{I_{\text{N}}}$

Table 1
Hyperfine constants, electric dipole moment and magnetic constants of $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ in the ground vibrational state

Constant	Present work	Others
$\mu_{e1}(\text{D})^{\text{a},\text{b}}$	2.83312(15)	2.80[15]
$eQ_{\text{Cl}}q_{\text{C}}^{\text{Cl}}(\text{kHz})$	-83275.19(40)	-83390(200)[20] -83285(20)[7]
$eQ_{\text{N}}q_{\text{C}}^{\text{N}}(\text{kHz})$	-3622.77(90)	-3370(260)[20] -3620(10)[7]
$c_{\text{C}}^{\text{Cl}}(\text{kHz})$	1.706(45)	3.0(15)[7]
$c_{\text{N}}^{\text{N}}(\text{kHz})$	1.32(18)	2.5(10)[7]
g_{\perp}	-0.04121(13)	-0.0385(2)[9] ^{c)}
$X_{\parallel} - X_{\perp}$ (10^{-30} J/T^2) ^{d)}	-184(2)	-179(8)[9] ^{e)}

^{a)} The reported value is an effective electric dipole moment. If the electric polarizability anisotropy is 10^{-29} m³ or less it can be regarded as the absolute value for the electric dipole moment. See also text.

^{b)} 1 D = 3.335641×10^{-30} Cm. ^{c)} For $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$.

^{d)} (10^{-30} J/T^2) = 0.0602205 (10^{-6} erg/G² mole).

$(1 - \sigma_{av}^N)$, $(\chi_{||} - \chi_{\perp})$, $(\sigma_{||} - \sigma_{\perp})^{Cl}$ and $(\sigma_{||} - \sigma_{\perp})^N$. The last two quantities could not be deduced from the observed spectra, while it was only possible to obtain a linear combination of $g_{I_{Cl}}(1 - \sigma_{av}^{Cl})$ and $g_{I_N}(1 - \sigma_{av}^N)$. However, the quantities g_{\perp} and $(\chi_{||} - \chi_{\perp})$ were well determined and the values are given in table 1.

4.2. Cyanogen chloride in the first excited bending vibrational state

In the (01^10) vibrational state of ClCN only l -doubling transitions ($\Delta J = 0$, $\Delta F = 0, \pm 1$) in the rotational states $J = 2$ and $J = 3$ in zero field have been observed. No transitions in the $J = 1$ state have been measured. The signal to noise ratios of the spectral lines were quite low. The vibrational effects on hyperfine levels were relatively small so that a unique interpretation of the $\nu_2 = 1$ spectrum gave no trouble. Table 2 lists all observed $J = 2$ and $J = 3$ transition frequencies. The experimental error for all lines was 0.25 kHz. The 53 lines of table 2 were used in fitting the l -doubling and hyperfine constants. In the least-squares fit d_T was again fixed at the calculated value of 0.039 kHz and anisotropies of the spin-rotation and spin-spin constants for directions perpendicular to the molecular axis were set equal to zero, since no significant improvement of the fit was achieved by adjusting them. Like in the case of N_2O [4] also for ClCN ten molecular constants could well be determined from the measured spectrum (see table 3).

The electric dipole moment of ClCN in the $\nu_2 = 1$ state was deduced from a measurement of seven transitions in the $J = 2$ state at a field strength of about 10 V/cm yielding a Stark shift of about 600 kHz. At higher electric field strengths the identification of the spectral lines became almost impossible because of the very low signal to noise ratios and the multiplicity of Stark components of the already rich zero field spectrum. The obtained value of the electric dipole moment is listed in table 3.

The low signal to noise ratios and complexity of the spectrum in an external magnetic field did not allow us to investigate the Zeeman spectrum in the $\nu_2 = 1$ state.

Table 2

Observed and calculated frequencies of $^{35}Cl^{12}C^{14}N$ in the $\nu_2 = 1$ state in zero external fields for $J = 2$ and 3. Experimental error is 0.25 kHz

J	F	\rightarrow	F'	Observed	Obs. - Calc.
2	7/2		5/2	44064.13	-0.23
	7/2		9/2	44212.42	-0.23
	7/2		7/2	44687.36	0.00
	9/2		9/2	44756.34	-0.21
	5/2		5/2	44782.30	-0.12
	9/2		7/2	45231.23	-0.03
	5/2		7/2	45405.38	-0.05
	5/2		7/2	42156.32	0.05
	5/2		5/2	41533.24	-0.03
	3/2		5/2	41552.84	-0.07
	7/2		5/2	47335.19	0.06
	5/2		3/2	48039.37	0.13
	5/2		5/2	48053.21	0.02
	5/2		5/2	44804.20	0.17
	3/2		3/2	44809.85	0.13
	1/2		3/2	52148.79	0.21
	5/2		3/2	52175.15	0.01
	3/2		3/2	52194.77	-0.01
	5/2		7/2	52233.54	-0.13
	5/2		5/2	52432.17	0.00
	3/2		5/2	52451.82	0.01
	7/2		7/2	54764.61	-0.15
	7/2		5/2	54963.17	-0.09
	9/2		7/2	55308.55	-0.11
	5/2		3/2	55424.32	0.03
	5/2		5/2	55681.30	-0.03
	3/2		3/2	55037.68	0.19
	3/2		5/2	55051.32	-0.12
	1/2		3/2	44763.89	0.37
	5/2		3/2	44790.24	0.16
	3/2		5/2	44824.05	0.37
	3/2		5/2	45238.53	-0.31
	3	5/2		5/2	89627.77
7/2			7/2	89666.04	0.06
3/2			3/2	89678.94	0.07
11/2			11/2	89551.60	-0.17
9/2			9/2	89474.39	-0.07
7/2			7/2	106067.73	-0.16
5/2			5/2	105500.13	0.22
7/2			5/2	105346.72	-0.03
11/2			9/2	105279.31	-0.08
5/2			7/2	105072.93	0.09
9/2			7/2	104977.47	0.04
3/2			3/2	104343.14	0.04
7/2			7/2	97516.52	-0.14
5/2			7/2	97051.10	-0.01
3/2			5/2	96964.20	-0.04
7/2		9/2	96930.72	-0.23	
7/2		5/2	96795.70	0.04	
5/2		5/2	96330.13	0.01	
11/2		9/2	90361.74	-0.40	
3/2		5/2	90261.73	0.10	
7/2		5/2	90093.31	0.26	

Table 3
Hyperfine constants (in kHz) and electric dipole moment (in D) of $^{35}\text{Cl}^{12}\text{C}^{14}\text{N}$ in the (01¹0) vibrational state

Constant	Present work	Others
q_v	7467.532(16)	7460.0(50)[21] 7467.467[22]
μ_v	-0.0183(15)	-0.01327[22]
$eQ_{\text{Cl}}q_{zz}^{\text{Cl}}$	-82815.54(55)	-82825(15)[7] ^{a)}
$eQ_{\text{Cl}}(q_{xx}^{\text{Cl}} - q_{yy}^{\text{Cl}})$	-927.84(49)	482(30)[7] ^{a,b)}
$eQ_{\text{N}}q_{zz}^{\text{N}}$	-3702.19(40)	
$eQ_{\text{N}}(q_{xx}^{\text{N}} - q_{yy}^{\text{N}})$	-256.00(41)	
$c_{\parallel\text{Cl}}^{\text{Cl}}$	1.695(48)	3.5(6)[7] ^{a)}
$c_{\perp\text{Cl}}^{\text{Cl}} - c_{\perp}^{\text{Cl}}$	7.38(35)	4.5(50)[7] ^{a)}
$c_{\parallel\text{N}}^{\text{N}}$	1.243(67)	
$c_{\perp\text{N}}^{\text{N}} - c_{\perp}^{\text{N}}$	2.20(53)	
$\mu_{\text{Cl}}(\text{D})$	2.804(3)	

^{a)} For ClC^{15}N . ^{b)} We believe that the $eQq_{\text{Cl}}\eta$ as defined in ref. [7] equals $-\frac{1}{2}eQ_{\text{Cl}}(q_{xx}^{\text{Cl}} - q_{yy}^{\text{Cl}})$.

5. Discussion

The molecular constants determined in the present work for ClCN in the ground vibrational state agree very well with the less accurate results of previous investigations. The same applies to the chlorine hyperfine constants and to the l -doubling constants q_v and μ_v . It should be noted that most of the constants available in the literature are for the ClC^{15}N isotopic species. The hyperfine constants in the excited state of the nitrogen (^{14}N) nucleus have been determined for the first time.

The magnetic constants of table 1 allow us to deduce the molecular quadrupole moment Θ_{\parallel} (component parallel to the molecular axis) using the relation [19]

$$\Theta_{\parallel} = -\frac{4m}{e}(\chi_{\parallel} - \chi_{\perp}) + \frac{h\mu_{\text{N}}g_{\perp}}{2\pi A} + me \sum_K \frac{Z_K r_K^2}{m_K}. \quad (6)$$

In this relation m and e represent the electron mass and the positive elementary charge, m_K is the mass and $Z_K e$ the charge of nucleus K in the molecule, r_K is the length of the position vector of nucleus K referred to the molecular center of mass, h is Planck's constant, μ_{N} is the nuclear magneton and A is the rotational constant of the molecule. The last contribution in eq. (6), being $0.018 \times 10^{-30} \text{ C m}^2$ can be neglected. Using the values of the magnetic

constants from table 1 and the internuclear distances of $1.631 \times 10^{-10} \text{ m}$ and $1.159 \times 10^{-10} \text{ m}$ [15] for Cl-C and C-N separation, respectively, we obtain for the electric quadrupole moment $\Theta_{\parallel} = -1.34(2) \times 10^{-30} \text{ C m}^2$. This value agrees very well with $-1.29(33) \times 10^{-30} \text{ C m}^2$ and $-1.34(33) \times 10^{-30} \text{ C m}^2$ obtained by Ewing et al. [9] for $^{35}\text{Cl}^{12}\text{C}^{15}\text{N}$ and $^{37}\text{Cl}^{12}\text{C}^{15}\text{N}$, respectively.

The paramagnetic part of the shielding anisotropies $(\sigma_{\parallel} - \sigma_{\perp})_{\text{Cl}}^{\text{p}}$ and $(\sigma_{\parallel} - \sigma_{\perp})_{\text{N}}^{\text{p}}$ can be deduced from the electronic part of the spin-rotation constants $(c_{\perp}^{\text{e}})_{\text{Cl}}$ and $(c_{\perp}^{\text{e}})_{\text{N}}$ using relation [19]

$$(2\mu_{\text{N}}g_{I_K}A/\mu_{\text{B}}) \times (\sigma_{\parallel} - \sigma_{\perp})_{\text{K}}^{\text{p}} = (c_{\perp}^{\text{e}})_{\text{K}}, \quad (7)$$

where g_{I_K} is the nuclear g_{\perp} -factor of nucleus K . The electronic contribution is found by subtracting the nuclear parts from the total (observed) spin-rotation constants. The last contribution is calculated from

$$(c_{\perp}^{\text{n}})_{\text{K}} = -\frac{e\mu_0\mu_{\text{N}}g_{I_K}A}{h} \sum_{L \neq K} \frac{Z_L}{r_{LK}^3} [r_{LK}^2 - \frac{1}{2}(x_{LK}^2 + y_{LK}^2)], \quad (8)$$

where $r_{LK} = |r_L - r_K|$, $x_{LK} = x_L - x_K$ and $y_{LK} = y_L - y_K$, $x_L(y_L)$ is the x -(y -) component of r_L , the position vector of nucleus L . For a linear molecule x_{LK} and y_{LK} are equal to zero. The nuclear contribution to the c_{\perp} -constants of ^{35}Cl and ^{14}N in ClCN is -0.310 kHz and -0.416 kHz , respectively. Combining the results from eq. (8) with those of table 1 the results for the paramagnetic parts of the shielding anisotropies are $(\sigma_{\parallel} - \sigma_{\perp})_{\text{Cl}}^{\text{p}} = 567(14) \text{ ppm}$ and $(\sigma_{\parallel} - \sigma_{\perp})_{\text{N}}^{\text{p}} = 663(76) \text{ ppm}$. The diamagnetic parts of the shielding anisotropies have been calculated by Gierke and Flygare using the atom-dipole method [11]: $(\sigma_{\parallel} - \sigma_{\perp})_{\text{Cl}}^{\text{d}} = -71 \text{ ppm}$ and $(\sigma_{\parallel} - \sigma_{\perp})_{\text{N}}^{\text{d}} = -125 \text{ ppm}$. The predicted total nuclear shielding anisotropies obtained by addition of the paramagnetic and diamagnetic parts are $(\sigma_{\parallel} - \sigma_{\perp})_{\text{Cl}} = 496 \text{ ppm}$ and $(\sigma_{\parallel} - \sigma_{\perp})_{\text{N}} = 538 \text{ ppm}$. Unfortunately we were not able to confirm these results experimentally (section 4.1).

Acknowledgement

The authors wish to thank Professor J. Reuss for helpful discussions. Technical assistance of Messrs. J. Holtkamp and C. Sikkens is greatly appreciated.

References

- [1] F.H. de Leeuw and A. Dymanus, *Chem. Phys. Letters* 7 (1970) 288.
- [2] J.M.L.J. Reinartz, W.L. Meerts and A. Dymanus, *Chem. Phys. Letters* 16 (1972) 576.
- [3] J.M.L.J. Reinartz and A. Dymanus, *Chem. Phys. Letters* 24 (1974) 346.
- [4] J.M.L.J. Reinartz, W.L. Meerts and A. Dymanus, *Chem. Phys.* 31 (1978) 19.
- [5] G.R. Tomasevich, Thesis, Harvard University (1970).
- [6] A.G. Maki, *Phys. Chem. Ref. Data* 3 (1974) 221.
- [7] R.L. White, *Rev. Mod. Phys.* 27 (1955) 276.
- [8] J.K. Tyler and J. Sheridan, *Trans. Faraday Soc.* 89 (1963) 2661.
- [9] J.J. Ewing, H.L. Tigelaar and W.H. Flygare, *J. Chem. Phys.* 56 (1972) 1957.
- [10] J.M.L.J. Reinartz, Thesis, Katholieke Universiteit, Nijmegen, The Netherlands (1976).
- [11] T.D. Gierke and W.H. Flygare, *J. Am. Chem. Soc.* 94 (1972) 7277.
- [12] A.R. Edmonds, *Angular momentum in quantum mechanics* (Princeton University Press, Princeton, 1960).
- [13] B.R. Judd, *Operator techniques in atomic spectroscopy* (McGraw-Hill, New York, 1963).
- [14] F.H. de Leeuw and A. Dymanus, *J. Mol. Spectry* 48 (1973) 427.
- [15] C.H. Townes and A.L. Schawlow, *Microwave spectroscopy* (McGraw-Hill, New York, 1955).
- [16] E.R. Cohen and B.N. Taylor, *J. Phys. Chem. Ref. Data* 2 (1973) 663.
- [17] R.A. Fisher and F. Yates, *Statistical tables for biological agricultural and medical research*, 6th Ed. (Oliver and Boyd, Edinburgh, 1963).
- [18] O.B. Dabbousi, W.L. Meerts, F.H. de Leeuw and A. Dymanus, *Chem. Phys.* 2 (1973) 473.
- [19] N.F. Ramsey, *Molecular beams* (Oxford University Press, New York, 1956).
- [20] W.J. Lafferty, D.R. Lide and R.A. Toth, *J. Chem. Phys.* 43 (1956) 2063.
- [21] C.A. Burrus and W. Gordy, *Phys. Rev.* 101 (1956) 599.
- [22] L. Yarmus, *Phys. Rev.* 105 (1957) 928.