The High-Frequency Rotational Spectrum of 1,1-Dichloroethylene

Z. Kisiel and L. Pszczółkowski

Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

Z. Naturforsch. **50a,** 347–351 (1995); received October 31, 1994

The *b*-type rotational spectrum of 1,1-dichloroethylene was investigated up to 450 GHz and was found to be dominated by type-II R-type bands. All constants in the sextic Hamiltonian for the ground states of the common isotopic species and of the ^{37}Cl isotopomer were determined from measurements on transitions with J up to 95. Quartic and sextic planarity defects were evaluated and are compared and discussed with those for several recently investigated planar molecules.

Key words: mm-wave rotational spectroscopy, band spectra, sextic constants.

Introduction

With the increasing importance of atmospheric studies at millimeter and infrared wavelengths the accurate knowledge of rotational spectra well into the submillimeter region becomes mandatory. The rotational spectrum of the volatile solvent 1,1-dichloroethylene has previously only been studied at frequencies below 70 GHz [1] with measurements for the common species taken up to $J=45$. The values of the nuclear quadrupole coupling constants and of the electric dipole moment are also known from the studies by Howe and Flygare [2, 3]. In the present work the coverage of the spectrum is extended by a factor of six in frequency and a factor of 2 in J through measurements with a BWO-based, source modulated spectrometer. Various tests are carried out to assess the reliability of the derived constants, and recent results for several molecules are collected to update the discussion of the higher order planarity defects to molecules higher than triatomic.

Experimental details

1,1-dichloroethylene of >99% purity was purchased from Merck and was used without further purification. Measurements were made on a room-temperature sample contained in a 10 cm diameter, 3.5 m long absorption cell. The spectrometer and the data manipulation techniques have been described previously [4–6] and allow, through the use of high-frequency BWO sources in free-running mode, a broadbanded, frequency agile coverage of frequencies up to ca. 500 GHz. Farran Technology SD-015 and SD-018 honeycomb Schottky diodes were used in the mixer for frequency measurement and in the detector, while for frequencies above 350 GHz a home-made superconducting InSb detector was preferred.

Results

The high frequency rotational spectrum of 1,1-dichloroethylene was found to be relatively sparse and dominated by type-II R-type bands. These bands are formed from near-coincidence of transitions between rotational energy levels that are the first to become degenerate in the direction of the oblate symmetric top limit. Thus the first line in each band will be formed from transitions between the level pairs $J_{0,J}$, $J_{1,J}$ and $J+1_{0,J+1}$, $J+1_{1,J+1}$ which are allowed by either μ_a or μ_b dipole moment component. The succeeding line will be formed from transitions between $J-1_{1,J-2}$, $J-1_{2,J-2}$ and $J_{1,J-1}$, $J_{2,J-1}$ levels, and for μ_b type transitions the quantum numbers of the two degenerate components of each line in the band will be given by

$$\begin{cases} j-k+1_{k+1,j-2k+1} \leftarrow j-k_{k,j-2k} \\ j-k+1_{k,j-2k+1} \leftarrow j-k_{k+1,j-2k} \end{cases}, \qquad (1)$$

where j is equal to J for the leading line in the band, and $k=0,1,2,3\ldots$. The overlap of μ_a $J+1_{0,J+1} \leftarrow J_{0,J}$ and $J+1_{1,J+1} \leftarrow J_{1,J}$ transitions was first noted by Borchert [7], who suggested the nomenclature 'type-II' to distinguish from the common ^{a}R bands formed from overlaps of various K_{-1} transitions for the same $J+1 \leftarrow J$. Extended type-II bands were observed in the

---

Reprint requests to Dr Z. Kisiel.

0932-0784 / 95 / 0400-0347 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

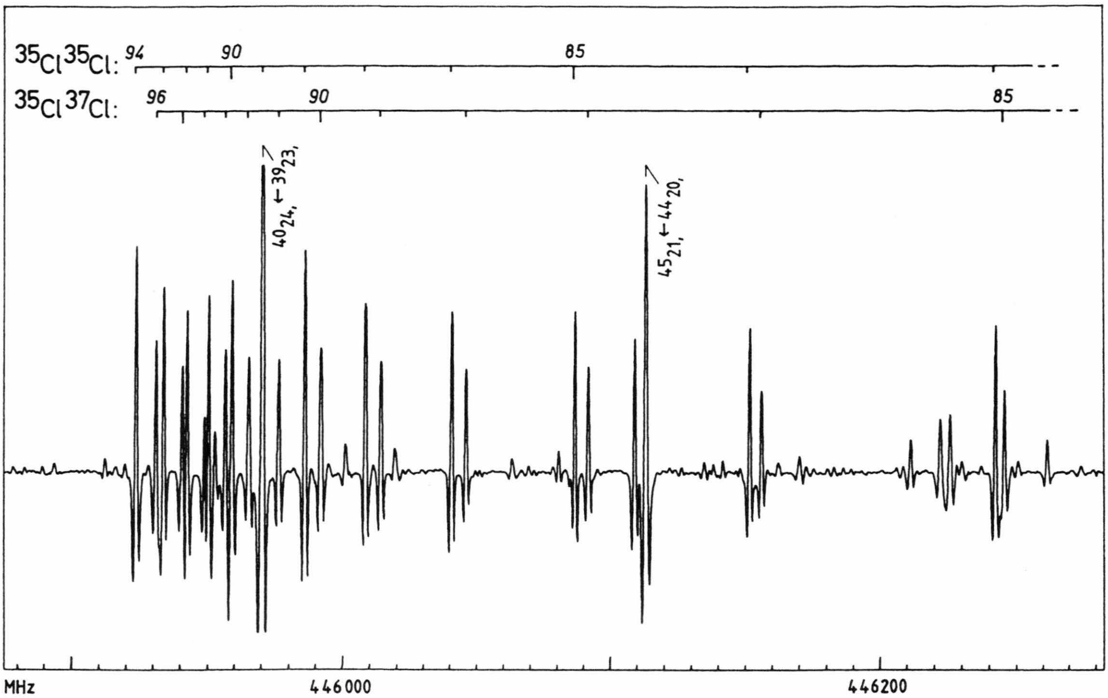

Fig. 1. The $j=94$ type-II R-type band of the common isotopic species of 1,1-dichloroethylene overlapped with the $j=96$ band of the ^{35}Cl^{37}Cl species. The constituent lines in these bands are each formed from a pair of $^bR_{1,1}$ and $^bR_{-1,1}$ transitions between asymmetric top level pairs which become degenerate at the oblate symmetric top limit. The leading line in the ^{35}Cl^{35}Cl band consists of overlapped $95_{1,95} \leftarrow 94_{0,94}$, $95_{0,95} \leftarrow 94_{1,94}$ transitions, and the value of J decreases by 1 between successive lines down the band. The values of J'' are marked for both bands. The spectrum was acquired using second harmonic detection with 4 kHz sinusoidal source modulation and did not require any background subtraction. The sample was at room temperature and pressure of 20 mTorr.

high-J μ_a spectrum of chlorobenzene [4], where it was established that the condition for their convergence was planarity of the molecule, the convergence limit being at the oblate symmetric top limit. It was shown that appreciable density of lines in such bands will be observed even for molecules with prolate asymmetry, providing that values of J will be sufficiently large. The relation between rotational constants of a planar molecule is $A+B=nC$ with $n=2+(3+\varkappa)/\sqrt{2(\varkappa+1)}$, and n was found to be a useful quantity for parameterising the expected convergence of type-II bands. At the convergence limit $n=4$ and its value increases with an increase in prolate character of asymmetry. Diagnostic plots of changes in frequency dispersion of leading lines in type-II bands as a function of J and of n have been provided in [4]. Subsequently we observed overlapped type-II μ_a and μ_b bands for 2-chloroacrylonitrile [8], and the present study reports the first observation of extensive bands of this type for a purely μ_b type spectrum. A specimen spectrum is reproduced in Fig. 1, in which je $j=94$ band of the common isotopic species is seen to overlap with the $j=96$ band of the ^{37}Cl species. Owing to the symmetry equivalence of the two chlorine atoms the intensity the ^{37}Cl isotopomer is 65% of the common species, so that its analysis becomes important for reproducing the whole spectrum. Even though the asymmetry parameter, $\varkappa$ for both isotopic species is near -0.6, the J reached in the spectrum in Fig. 1 is sufficient for the essentially oblate type-II bands to converge to the degree that the first twelve lines fall within 300 MHz.

The band lines define only a subset of the constants in the Hamiltonian, so that they were augmented by measurements on the non-band R-type lines such as the two strong lines visible in Fig. 1, and also by Q-type transitions with values of K_{-1} ranging from 1 to 50. The values of J exceed 90 for both R- and Q-type transitions. Tables of measured frequencies for the common and for the ^{37}Cl species are available from the authors. In the analysis our measurements were

Table 1. Spectroscopic constants for the ground state of ^{35}Cl^{35}Cl and ^{35}Cl^{37}Cl isotopic species of 1,1-dichloroethylene in Watson's Hamiltonian, reduction A.

		$H_2C=C\,^{35}Cl^{35}Cl$		$H_2C=C\,^{35}Cl^{37}Cl$	
		Ref. [1]	This work	Ref. [1]	This work
A	(MHz)	7467.0809 (15)[a]	7467.08368 (52)	7424.0608 (27)	7424.06593 (74)
B	(MHz)	3411.56017 (64)	3411.56106 (29)	3319.4231 (12)	3319.42552 (41)
C	(MHz)	2339.08249 (62)	2339.08300 (23)	2291.2986 (13)	2291.30229 (30)
Δ_J	(kHz)	0.90039 (42)	0.901667 (76)	0.8484 (39)	0.85639 (14)
Δ_{JK}	(kHz)	−1.2328 (44)	−1.23827 (22)	−1.164 (18)	−1.19354 (47)
Δ_K	(kHz)	8.3115 (21)	8.31771 (38)	8.200 (24)	8.2414 (11)
δ_J	(kHz)	0.32978 (47)	0.329162 (29)	0.3130 (17)	0.309649 (61)
δ_K	(kHz)	1.7894 (71)	1.81534 (35)	1.694 (34)	1.7600 (11)
Φ_J	(Hz)		0.0005998 (85)		0.000251 (20)
Φ_{JK}	(Hz)		0.004625 (82)		0.00131 (15)
Φ_{KJ}	(Hz)	−0.0253 (21)	−0.03235 (31)	[b]	−0.01917 (65)
Φ_K	(Hz)	0.0452 (14)	0.05351 (26)	[b]	0.04388 (83)
ϕ_J	(Hz)	0.00025 (16)	0.0003029 (40)	[b]	0.0001320 (98)
ϕ_{JK}	(Hz)	−0.0059 (21)	0.002975 (68)	[b]	−0.00020 (18)
ϕ_K	(Hz)		0.02743 (46)		0.0048 (10)
lines fitted		76	259	37	205
σ_{fit}	(MHz)	0.031	0.069	0.045	0.080
σ_{w}^{c}			0.751		0.879

[a] Uncertainties are standard errors in units of the last quoted digit.
[b] Assumed to be the same as in $H_2C=C\,^{35}Cl^{35}Cl$.
[c] Deviation of fit per unit weight.

combined with those from [1], and spectroscopic constants resulting from a fit of Watson's A, I^r Hamiltonian are reported in Table 1. The comparison with previous values shows improvement in accuracy of all constants. In particular, full sets of sextic constants have been determined for the first time for both isotopic species. The data have also been fitted with the S-reduced form of Watson's Hamiltonian, which is sometimes preferred on account of the somewhat smaller intercorrelations between constants, even for molecules which are not very close to the symmetric top limits. For 1,1-dichloroethylene the A- and S-type fits result in identical standard deviations but the latter does indeed confer a slight advantage in intercorrelations. This is evident from the average values of the absolute correlation coefficient, $\overline{|C_{ij}|}$, for the fits, which for the common and the ^{37}Cl species are respectively 0.373 and 0.472 for the A-type fit, and 0.321 and 0.362 for the S-type fit. The fitted S-reduction constants are reported in Table 2, where they are also compared with the values calculated from the fitted A-type constants by using an inversion of the relations given in [9]. The recalculated values have been assigned errors determined by carrying out error propagation with the aid of a symbolic calculations programme. Since the relations between the A- and S-type constants have been derived with the assumption of a sextic level Hamiltonian, the comparison between the fitted and the calculated constants provides a useful test of whether there are any effective contributions from higher orders to fitted constants. The satisfactory agreement visible in Table 2 shows that this is not the case, although the beginnings of discrepancies may be visible for some constants of the common species, for which there is a larger data set to be fitted.

Discussion

The spectroscopic constants for 1,1-dichloroethylene determined here should facilitate accurate prediction of the principal features of the rotational spectum of this molecule to considerably higher frequencies than in the present measurements. At high J the contributions to frequencies of the leading lines in type-II bands reduce to those from only a limited number of constants, in the sequence C, Δ_J, δ_J, Φ_J, ϕ_J.... We have, for example, recently observed that for chlorobenzene the frequences of the first ten lines of the $j=175$ band

Table 2. Spectroscopic constants for the common species and the ^{37}Cl isotopomer of 1,1-dichloroethylene in Watson's Hamiltonian, reduction S. The fitted constants are compared with values calculated from the A-reduction constants.

		$H_2C=C\,^{35}Cl^{35}Cl$		$H_2C=C\,^{35}Cl^{37}Cl$	
		Fitted	Calculated[a]	Fitted	Calculated[a]
A	(MHz)	7467.08424 (52)	7467.08421 (52)	7424.06639 (74)	7424.06642 (74)
B	(MHz)	3411.55728 (29)	3411.55722 (29)	3319.42180 (41)	3319.42181 (41)
C	(MHz)	2339.08649 (23)	2339.08642 (23)	2291.30562 (30)	2291.30562 (30)
D_J	(kHz)	0.795724 (70)	0.795667 (79)	0.758454 (95)	0.758445 (147)
D_{JK}	(kHz)	−0.60232 (24)	−0.60227 (25)	−0.60595 (51)	−0.60586 (59)
D_K	(kHz)	7.78766 (39)	7.78771 (40)	7.7518 (11)	7.7517 (11)
d_1	(kHz)	−0.329165 (29)	−0.329162 (29)	−0.309650 (61)	−0.309649 (61)
d_2	(kHz)	−0.052986 (10)	−0.053000 (10)	−0.048969 (29)	−0.048973 (30)
H_J	(Hz)	0.0002653 (63)	0.0002571 (94)	0.000126 (11)	0.000124 (23)
H_{JK}	(Hz)	0.002026 (37)	0.001962 (116)	0.001266 (70)	0.001280 (236)
H_{KJ}	(Hz)	−0.01855 (12)	−0.01833 (41)	−0.01720 (33)	−0.01718 (87)
H_K	(Hz)	0.04263 (14)	0.04250 (32)	0.04209 (70)	0.04204 (92)
h_1	(Hz)	0.0002703 (37)	0.0002685 (40)	0.0001268 (89)	0.0001265 (99)
h_2	(Hz)	0.0001687 (21)	0.0001714 (20)	0.0000626 (53)	0.0000633 (51)
h_3	(Hz)	0.00003365 (57)	0.00003445 (58)	0.0000053 (12)	0.0000055 (12)

[a] Calculated from the A-reduction constants in Table 1.

Table 3. Comparison of the quadratic, Δ_i (uÅ^2), quartic, Δ_q (MHz^2), and sextic, Δ_s (kHz^2) inertial defects for various molecules.

	T_2O, Ref. [10]	O_3, Ref. [11]	ONF, Ref. [12]	SO_2, Ref. [13]	$H_2C=CHCN$, Ref. [14]
C (GHz)	100.2594	11.8344	10.5082	8.7997	4.5138
Δ_i	0.079637 (1)[a]	0.102427 (3)	0.116201 (4)	0.136304 (3)	0.16343 (1)
Δ_q	0.1838 (6) × 10^6	24.80 (5)	12.5 (1)	8.65 (2)	2.27 (3)
Δ_s	63 (18) × 10^6	−495 (45)[b]	578 (111)	−70 (12)[b]	177 (53)
$\Delta_q/(4C\Delta_J)$	0.1106 (3)	0.03849 (7)	0.0152 (1)	0.0372 (1)	0.0561 (7)
$\Delta_s/(6C\Phi_J)$	0.19 (5)	−0.97 (9)	−1.6 (3)	−0.12 (2)	1.1 (3)

	$HC\equiv CCOOH$, Ref. [15]	*cis*-HClC=CFH Ref. [16]	$H_2C=CCl_2$, this work	$H_2C=CClCN$, Ref. [8]	*cis*-HClC=CClH, Ref. [17]
C (GHz)	3.0844	3.0529	2.3391	2.1652	2.0826
Δ_i	0.24521 (1)	0.19869 (2)	0.24052 (2)	0.32314 (4)	0.23138 (4)
Δ_q	0.341 (3)	0.31 (3)	0.041 (1)	0.096 (3)	0.072 (2)
Δ_s	0.7 (15)	−13 (17)	0.25 (29)	2.3 (7)	−0.4 (6)
$\Delta_q/(4C\Delta_J)$	0.0501 (5)	0.0086 (8)	0.0048 (1)	0.0102 (3)	0.0060 (2)
$\Delta_s/(6C\Phi_J)$	0.1 (5)	−0.2 (2)	0.03 (3)	0.07 (2)	−0.03 (5)

[a] Errors are standard errors in units of the last quoted digit.

[b] Previous values, O_3: $\Delta_s = 41$ (820) kHz^2, SO_2: $\Delta_s = -324$ (168) kHz^2, [9].

at 435 GHz showed a systematic shift of only 50 kHz relative to predictions based on data up to $j = 104$ and 260 GHz.

Accurate sextic level constants have recently been determined for several planar molecules, including some comparable in size to 1,1-dichloroethylene. The behaviour of the quadratic planarity defect, Δ_i, has seen much analysis, whereas the properties of the higher quartic Δ_q, and sextic Δ_s, defects are less well known. For reduction-A, representation-I^r of Watson's Hamiltonian the two higher defects are given by

$$\Delta_q = 4C\Delta_J - (B-C)\Delta_{JK} - 2(2A+B+C)\delta_J + 2(B-C)\delta_K\,, \qquad (2)$$

$$\begin{aligned}\Delta_s &= 6C\Phi_J - (B-C)\Phi_{JK} - 2(2A+B+3C)\phi_J \\ &\quad + 2(B-C)\phi_{JK}, \\ &\quad + 4\Delta_J^2 - 4\delta_J(4\Delta_J+\Delta_{JK}-2\delta_J-2\delta_K). \quad (3)\end{aligned}$$

Watson's analysis for several triatomic molecules [9] showed that while the quartic defect is determinable, the sextic defect is on the verge of being significant. Table 3 reports values of planar defects for 1,1-dichloroethylene, together with values calculated from recently determined A, I^r Watsonian constants for several molecules. The listing is ordered according to decreasing C, which provides a measure of the increase in size of the planar molecules. All of these molecules are of appreciable prolate symmetry, with $\varkappa < -0.5$, and the quadratic defect shows a perceptible increasing trend down the table. This can be rationalised by an increase in the size of harmonic vibration-rotation inertial contributions in larger molecules, due to the larger number of vibrational modes and a decrease in the frequencies of the lowest frequency modes. The ordering of molecules in the table is also seen to correspond roughly to decreasing Δ_q and Δ_s. The two higher defects for 1,1-dichloroethylene are somewhat lower than those for the two largest molecules in the table which, in the first approximation, may be attributed to the more compact heavy atom arrangement in this molecule.

Table 3 shows that Watson's conclusion regarding borderline determinability of Δ_s is still valid for the heavier molecules, whereas for the lighter molecules in the first row of the table the level of significance in Δ_s is higher and currently near 10% for O_3. It is of interest to establish what is the degree of cancellation of terms determining Δ_q and Δ_s, and how these quantities scale relative to the size of related spectroscopic constants. It seems natural to use the first terms of (2) and (3) for such scaling, and for this reason the quantities $\Delta_q/(4C\Delta_J)$ and $\Delta_s/(6C\Phi_J)$ are also listed in Table 3. For the heaviest molecules the quartic defect is found to be from one to two hundred times smaller than $4C\Delta_J$, whereas the ratio involving the sextic defect is smaller as Δ_s does not fall much below a tenth of $6C\Phi_J$. In summary, Table 3 provides a ready basis for a first estimate of the size of the higher order defects for a wide range of prolate molecules, and for the heaviest molecules currently under study Δ_s is expected to be below 1 kHz^2 and Δ_q below 0.1 MHz^2. The underlying causes for variation in these quantities will, at a more subtle level, differ from molecule to molecule, but the steady decrease in the ratios $\Delta_q/(4C\Delta_J)$ and $\Delta_s/(6C\Phi_J)$ with molecular size suggests that the applicability of the Hamiltonian increases.

In addition to the evaluation of Δ_q and Δ_s it is possible to use relations (2)–(3) and the assumption of zero defect to determine any one of the four centrifugal distortion constants of a given level from the remaining three. For 1,1,-dichloroethylene the constants evaluated in this way differ from the experimental values by 0.5, −0.3, 3.1, 1.1% for Δ_J, δ_J, Δ_{JK}, δ_K and 3.0, −1.7, −5.1, 4.0% for Φ_J, ϕ_J, Φ_{JK}, ϕ_{JK}. The sextic constants for this molecule appear therefore to be very well behaved and can be expected to provide useful additional information on its anharmonic potential [18].

Acknowledgements

We are grateful to Prof. G. Cazzoli of University of Bologna for the InSb chip used in the detector. This work was supported from the research grant KBN 0-0487-91-01 and the Institute of Physics Research Project No. 6.

[1] R. Wellington Davis and M. C. L. Gerry, J. Mol. Spectrosc. **102,** 297 (1983).
[2] J. A. Howe and W. H. Flygare, J. Chem. Phys. **36,** 440 (1962).
[3] J. A. Howe and W. H. Flygare, J. Chem. Phys. **36,** 650 (1962).
[4] Z. Kisiel, J. Mol. Spectrosc. **144,** 381 (1990).
[5] Z. Kisiel, J. Mol. Spectrosc. **151,** 396 (1992).
[6] Z. Kisiel and L. Pszczółkowski, J. Mol. Spectrosc. **158,** 318 (1993).
[7] S. J. Borchert, J. Mol. Spectrosc. **57,** 312 (1975).
[8] Z. Kisiel and L. Pszczółkowski, J. Mol. Spectrosc. **166,** 32 (1994).
[9] J. K. G. Watson, J. Mol. Spectrosc. **65,** 123 (1977).
[10] F. C. De Lucia, P. Helminger, W. Gordy, H. W. Morgan, and P. A. Staats, Phys. Rev. **A8,** 2785 (1973).
[11] M. Bellini, P. De Natale, G. Di Lonardo, L. Fusina, M. Inguscio, and M. Prevedelli, J. Mol. Spectrosc. **152,** 256 (1992).
[12] G. Cazzoli, C. Degli Esposti, P. G. Favero, and P. Palmieri, Nuovo Cim. **3D,** 627 (1984).
[13] P. A. Helminger and F. C. De Lucia, J. Mol. Spectrosc. **111,** 66 (1985).
[14] G. Cazzoli and Z. Kisiel, J. Mol. Spectrosc. **130,** 303 (1988).
[15] G. Wlodarczak, D. Boucher, J. Burie, and J. Demaison, J. Mol. Spectrosc. **123,** 496 (1987).
[16] J. L. Alonso, A. G. Lesarri, A. L. Leal, and J. C. Lopez, J. Mol. Spectrosc. **162,** 4 (1993).
[17] L. A. Leal, J. L. Alonso, and A. G. Lesarri, J. Mol. Spectrosc. **165,** 368 (1994).
[18] Y. Yamaoka and K. Machida, J. Mol. Spectrosc. **83,** 21 (1980).