

Terahertz rotational spectra of NH_2OH in the ground and some low excited vibrational states[☆]

I. Morino^a, K.M.T. Yamada^{a,*}, H. Klein^b, S.P. Belov^b, G. Winnewisser^b, R. Bocquet^c,
G. Wlodarczak^c, W. Lodyga^{c,d}, M. Kreglewski^d

^aNational Institute for Advanced Interdisciplinary Research (NAIR), Tsukuba 305-8562, Japan

^bI. Physikalisches Institut, Universität zu Köln, D-50937 Cologne, Germany

^cLaboratoire de Physique des Lasers, Atomes et Molécules, Université des Sciences et Technologies de Lille,
F-59655 Villeneuve D'Ascq Cedex, France

^dFaculty of Chemistry, Adam Mickiewicz University, PL 60-780 Poznan, Poland

Received 11 January 1999; accepted 4 March 1999

Abstract

The rotational spectra of hydroxylamine, NH_2OH , have been measured for the ground and some excited vibrational states, with high precision in the mmW (millimeter wave) and sub-mmW region, up to 1.8 THz, using BWO based spectrometers and a laser-side-band FIR spectrometer. No tunnel splitting has been observed and it is concluded that the barrier to the tunneling motion is very high. The observed line positions have been analyzed with Watson's S -reduced Hamiltonian with extension to higher order terms up to J^{10} order. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NH_2OH ; Hydroxylamine; Terahertz spectroscopy; Millimeter-wave spectroscopy

1. Introduction

The two functional groups, $-\text{NH}_2$ and $-\text{OH}$, often exhibit large amplitude vibrational motions, i.e. inversion of the NH_2 unit and torsion of the OH part. Hydroxylamine, NH_2OH , is composed only of these two functional groups, and only few spectroscopic studies have been carried out with the interest on the intramolecular motions.

The molecular structure of hydroxylamine was determined by Tsunekawa [1] by MW (microwave)

spectroscopy. He reported the r_0 -structure obtained from the rotational constants of the parent isotopomer and five deuterated isotopomers. The *anti*-conformer was found to be stable in the gas phase (see Fig. 1); the hydrogen atoms of the $-\text{NH}_2$ and $-\text{OH}$ groups facing opposite direction, and the plane determined by N–O–H, i.e. a – c plane, bisects the angle H–N–H. The a -component of the dipole moment is larger than the c -component; $\mu_a = 0.586$ D and $\mu_c = 0.060$ D [1]. Recently, Luckhaus [2] measured rovibrational spectra of this molecule by high resolution FTIR (Fourier Transform Infrared) spectroscopy for a number of bands from 800 to 10 500 cm^{-1} . A good summary of the spectroscopic studies on this molecule published previously are given in his paper. We only wish to mention here the most recent work in the FIR (far infrared) region by Hanoune et al. [3].

[☆] In honour of Dr. Georges Graner for his many contributions to science.

* Corresponding author. Tel.: + 81-298542541; fax: + 81-298542549.

E-mail address: kyamada@nair.go.jp (K.M.T. Yamada).

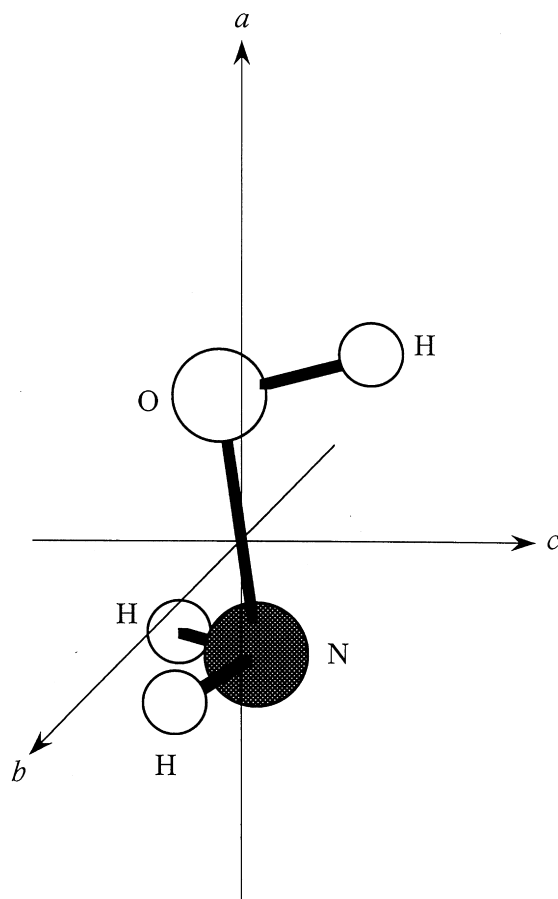


Fig. 1. Structure of the hydroxylamine molecule, in *anti*-conformation, is illustrated with the three principal axes. The molecule is of C_s symmetry, and the permanent dipole moment is in the a - c plane.

Luckhaus [2] also discussed the molecular structure and the large amplitude motions, on the basis of the quantum-chemical calculations. Fig. 2 illustrates the four conformers of NH_2OH , which are expected to be stable. Luckhaus' calculations predict that the *anti*-conformers, I and its mirror image I' , are the stable structures and the *syn*-conformers, II and its mirror image II' , are the metastable ones; *syn*-conformer is energetically higher than *anti* by about 2000 cm^{-1} . The *syn*-*anti* isomerization is predicted to occur through two paths: the inversion of $-\text{NH}_2$ (barrier height of $\sim 5000\text{ cm}^{-1}$) and the torsion of $-\text{OH}$ (barrier height of 2900 cm^{-1}).

The tunneling between the equivalent conformers I and I' , or II and II' , should result in the splitting of the

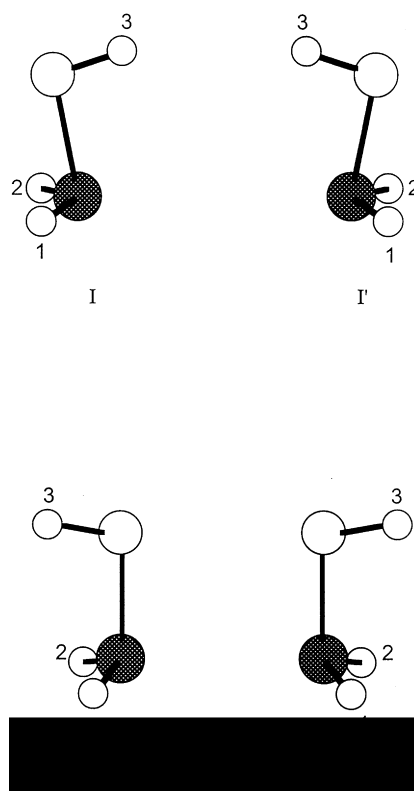


Fig. 2. Four possible conformers of the hydroxylamine molecule are illustrated. I and I' represent the *anti*-conformers, and are mirror image of each other. II is a *syn*-conformer and II' is its mirror image. The tunneling between I and I' , or II and II' , should remove the degeneracy of the mirror image states.

energy levels. The path for such tunneling is the combination of inversion and torsion. According to the Luckhaus' calculation, the barrier for such motion is very high and no observable splitting is expected. The two dimensional potential surface at MP2 level was calculated by Makarewicz et al. [4]; they have studied the coupled torsional and wagging motions using the calculated potential surface.

In the present study, we have measured pure-rotational spectra of NH_2OH with high-resolution; i.e. with Doppler-limited resolution in the sub-mmW region. One of the purposes of the present study is to provide an experimental support for the high barrier to the tunneling motion predicted by the calculations. The second purpose is to supply accurate sets of spectroscopic parameters of the molecule, which may be useful for the radio-astronomical search and

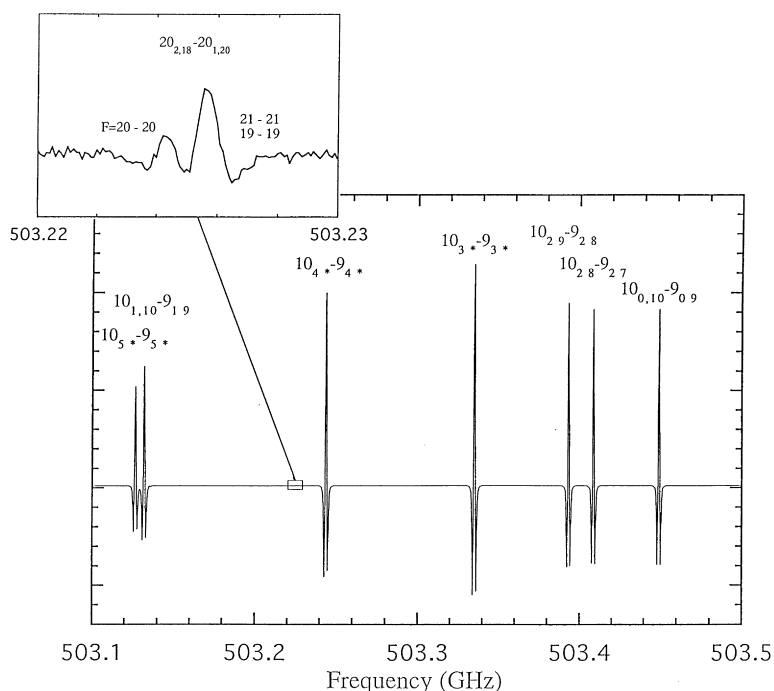


Fig. 3. A portion of the observed spectra is reproduced for the frequency range from 503.1 to 503.5 GHz. The lines were recorded in the second derivative form by using the source frequency modulation. The *a*-type transitions have been observed to be very strong. The weak line near 503.2 GHz is a *c*-type transition, which is shown in an expanded scale. For the unresolved *K*-type doublets the quantum numbers K_c are indicated by *.

for developing new FIR lasers [5]. Besides NH_3 , only few molecules containing NH_2 group have been detected in interstellar space; NH_2CHO , CH_3NH_2 , NH_2CN , NH_2 , and NH_2^+ . NH_2OH is of astrophysical interest, especially for tracing the chemical evolution in space from small molecules to large biological molecules.

The lines have been identified and analyzed in the present study for the ground state, $\nu_9 = 1$ and 2, and $\nu_6 = 1$ states. The ν_9 and ν_6 are the vibrational modes of the lowest frequencies: ν_9 (OH torsion) = 385.96 cm^{-1} [3] and ν_6 (NO stretching) = 895.21 cm^{-1} [2].

2. Experimental procedures

The measurements were carried out in three laboratories. At NAIR, the rotational spectra were recorded in the mmW (millimeter wave) and sub-mmW region from 250 to 750 GHz using Russian BWOs. At the

University of Cologne, the terahertz spectra were recorded in the region from 900 to 1100 GHz, also using Russian BWOs. The details of those NAIR and Cologne spectrometers are given elsewhere [6,7]. At the University of Lille, the mmW and sub-mmW spectra in the region from 150 to 500 GHz were observed by a Carcinotron-based spectrometer [8], and those from 500 to 1800 GHz by a laser-side-band spectrometer [9].

Essentially the same procedures were applied in the three laboratories for the production and the handling of the sample in the present study. In the following, the procedure used in NAIR is described. The gaseous hydroxylamine was produced by pyrolysis of phosphate salt, $(\text{NH}_2\text{OH})_3\text{H}_3\text{PO}_4$ [10]. The salt powder was placed in a pyrex-glass tube, outer-diameter of 40 mm, which was heated by an electric heating tape to a temperature of $\sim 80^\circ\text{C}$ using a thermostat. The length of the heated region was 100 mm. The evaporated sample gas was introduced to the absorption cell (1 m long) without any additional carrier gas.

Table 1

Number of lines used in the present analysis. (Total number of lines included in the fit for each state; an unresolved K-doublet is counted as two lines. The data in the column “MW” is taken from Ref. [1]. The data in column “NAIR” and “Cologne” are the present data from NAIR and Cologne. The data in the column “Lille-L” are from Lille for the frequency lower than 500 GHz, and “Lille-H” higher than 500 GHz. In the last column the standard deviation of the final fit (1σ) is given)

Vibrational state	Total	MW	NAIR	Lille-L	Lille-H	Cologne	σ/kHz
Ground State	341	13	101	93	89	45	75.0
$\nu_9 = 1$	308	1	117	76	16	98	60.5
$\nu_9 = 2$	163	1	86	76	0	0	60.8
$\nu_6 = 1$	123	0	60	63	0	0	98.2

The cell was continuously evacuated by a rotary pump through a liquid N₂ cooled trap. The pumping speed was adjusted so that the cell pressure was kept at about 30 mTorr (1 Torr = 133.322 Pa) measured at the exhaust port of the cell.

3. Observed spectra and analysis

As expected from the values of the dipole moment components, we have observed a large number of strong a-type transitions and a few weak c-type transitions, which exhibit several orders of magnitude lower line intensities than the a-type spectra display. A typical sub-mmW spectra observed in NAIR is reproduced in Fig. 3, where both a- and c-type transitions can be seen. In addition to the ground state transitions, we could identify in the present study transitions assigned to the $\nu_9 = 1$ and 2, and to the $\nu_6 = 1$ excited vibrational states. At an early stage of this study, the assignments have been carried out by the line positions predicted from the data of FTIR spectra [2,3]. Later on, the predictions have been improved stepwise by fitting the newly obtained data.

The observed transitions are listed in Table 1. In the present work, any splitting due to a tunneling motion between two equivalent potential minima has not been detected.

The a-type transitions with $J \approx K_a$ exhibit hyperfine splitting due to the nuclear quadratic moment of the ¹⁴N nucleus. Hyperfine splittings are also observed for most of the c-type transitions as shown in Fig. 3. In cases where the hyperfine splitting has been observed, the unsplit line position is estimated as an average weighted by the expected line intensities of each component. The analysis of the hyperfine splitting

has not been carried out in the present study, because the nuclear quadrupole coupling constants were determined accurately by Tsunekawa's MW study [1].

The observed line positions have been reproduced by a standard Watson-type *S*-reduced Hamiltonian for asymmetric-tops [11],

$$\begin{aligned} \hat{H}_{\text{rot}}^S = & \frac{1}{2}(\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)})\hat{J}^2 + \left\{ \tilde{B}_x^{(S)} - \frac{1}{2}(\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)}) \right\} \hat{J}_z^2 \\ & - D_J \hat{J}^4 - D_{JK} \hat{J}^2 \hat{J}_z^2 - D_K \hat{J}_z^4 + H_J \hat{J}^6 + H_{JK} \hat{J}^4 \hat{J}_z^2 \\ & + H_{KJ} \hat{J}^2 \hat{J}_z^4 + H_K \hat{J}_z^6 \\ & + \left\{ \frac{1}{4}(\tilde{B}_x^{(S)} - \tilde{B}_y^{(S)}) + d_1 \hat{J}^2 + h_1 \hat{J}^4 \right\} (\hat{J}_+^2 + \hat{J}_-^2) \\ & + (d_2 \hat{J}^2 + h_2 \hat{J}^4) (\hat{J}_+^4 + \hat{J}_-^4) + h_3 (\hat{J}_+^6 + \hat{J}_-^6) \end{aligned} \quad (1)$$

with extension up to J^{10} terms [12]:

$$\begin{aligned} \hat{H}' = & -L_J \hat{J}^8 - L_{62} \hat{J}^6 \hat{J}_z^2 - L_{44} \hat{J}^4 \hat{J}_z^4 - L_{26} \hat{J}^2 \hat{J}_z^6 - L_K \hat{J}_z^8 \\ & + S_J \hat{J}^{10} + S_{82} \hat{J}^8 \hat{J}_z^2 + S_{64} \hat{J}^6 \hat{J}_z^4 + S_{46} \hat{J}^4 \hat{J}_z^6 \\ & + S_{28} \hat{J}^2 \hat{J}_z^8 + S_K \hat{J}_z^{10} + (\ell_1 \hat{J}^6 + s_1 \hat{J}^8) (\hat{J}_+^2 + \hat{J}_-^2) \\ & + (\ell_2 \hat{J}^4 + s_2 \hat{J}^6) (\hat{J}_+^4 + \hat{J}_-^4) + (\ell_3 \hat{J}^2 + s_3 \hat{J}^4) (\hat{J}_+^6 + \hat{J}_-^6) \\ & + (\ell_4 + s_4 \hat{J}^2) (\hat{J}_+^8 + \hat{J}_-^8). \end{aligned} \quad (2)$$

In this Hamiltonian, the centrifugal terms starting with capital letters represent diagonal terms and with lower case letters off-diagonal terms. The diagonal centrifugal terms are defined by following the sign convention of alternative polynomials; i.e. *D* and *L* terms appear with negative sign in the above equation.

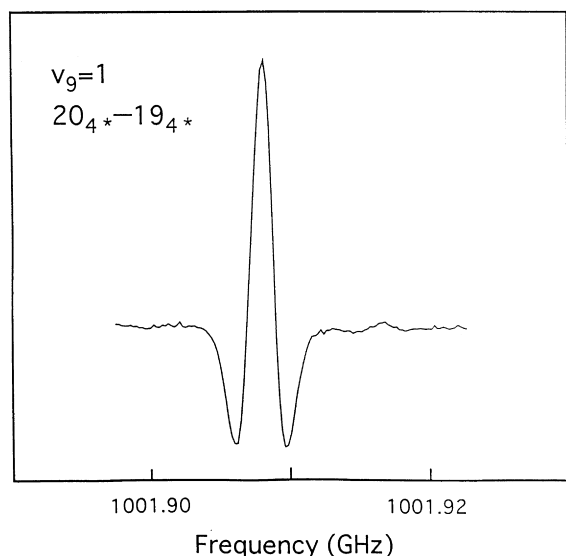


Fig. 4. A portion of the terahertz spectra observed in Cologne is reproduced, which shows the transition in the $v_9 = 1$ excited state. As the K -type doubling is not resolved the quantum number K_c is indicated by *.

The off-diagonal terms are defined always with positive sign.

The rotational and centrifugal distortion constants, including some higher order terms, have been determined by a least-squares fit using the presently observed line positions and the previously reported MW (microwave) data [1]. As we have five data sets with different experimental accuracy, a weighted least-squares analysis has been carried out; the weight for each line was given to be proportional to the reciprocal square of expected experimental uncertainty. The experimental uncertainties are estimated to be 200 kHz for the MW lines, 50 kHz for the lines measured in NAIR, and 500 kHz for the terahertz lines measured in Cologne. For the lines measured in Lille, the uncertainty of 50 kHz is assumed for the lines lower than 500 GHz, and 500 kHz for the lines higher than 500 GHz. For the lines in the terahertz region, the experimental uncertainty varies from line to line mainly due to the unleveled baseline. The numbers assumed above are the expected average errors. An example of a more precise terahertz measurement is shown in Fig. 4; the line position of this line may be determined as accurate as 50 kHz.

In the least-squares fit program, a dimensionless weight factor is introduced by normalizing the sum of the weights to be equal to the number of independent measurements [13]. Lines with partially resolved K -type structure and those with observed hyperfine splitting were assigned large uncertainties.

The spectroscopic parameters determined in the present study for the ground, $v_9 = 1$ and 2, and $v_6 = 1$ states are listed in Table 2. Up to J^8 terms, the diagonal and off-diagonal parameters are adjusted in the fit procedure. The J^{10} terms are included only for the diagonals. In case the absolute value of a parameter is determined to be less than 1σ , the parameter is assumed to be zero in the final fits. The rotational constants, A , B and C , obtained in the present study for the ground, and $v_9 = 1$ and 2 states agree with those reported in Ref. [3] within 3σ . The values for the $v_6 = 1$ state also agree well with those reported in Ref. [2]. The orders of magnitude of the centrifugal distortion constants are also in agreement, although much more parameters have been adjusted in the present study. The list of the observed transition frequencies is available from the authors upon request.

4. Discussion

The molecule was found to be not so floppy as we had expected. The spectra so far observed exhibit no splitting due to the tunneling effect even for the excited torsional states up to $v_6 = 1$, including $v_9 = 2$. The experimental results strongly support the theoretical calculations, which predicted the potential barrier for the tunneling motion to be very high [2,4]. The path connecting the equivalent configurations cannot be expressed by a single normal mode but requires the combination of the torsional and inversional modes. Therefore, the tunnel splitting may be observed for excited combination states, such as $(v_6, v_9) = (1, 1)$. The rotational lines of those highly excited states have, however, not been identified yet.

Many higher order terms in the effective rotational Hamiltonian are required to reproduce the observed rotational line positions even for the ground state. The parameters up to the quartic centrifugal distortion constants seem to be consistent for the ground and the three excited states. Many of the higher order

Table 2

The spectroscopic constants of NH_2OH determined in the present study (numbers in parentheses are one standard deviations in unit of the last digit)

Parameter	G.S.	$v_9 = 1$	$v_9 = 2$	$v_6 = 1$	Unit
A	190976.1802(83)	189692.826(15)	188644.333(15)	190446.713(68)	MHz
B	25218.7364(16)	25210.7936(12)	25199.0474(19)	24903.4933(96)	MHz
C	25156.5511(15)	25022.6310(14)	24895.3883(25)	24846.1936(86)	MHz
D_J	75.1464(79)	74.0441(94)	73.335(22)	75.61(21)	kHz
D_{JK}	650.938(91)	619.853(87)	599.53(31)	661.8(11)	kHz
D_K	3.55456(53)	3.3591(18)	3.20426(92)	3.649(14)	MHz
d_1	−1.1276(38)	−1.3350(22)	−1.5947(14)	−1.0855(56)	kHz
d_2	1.59555(89)	1.6144(11)	1.5841(31)	1.551(11)	kHz
H_J	−0.044(22)	−0.807(32)	−1.069(78)	5.3(21)	Hz
H_{JK}	−0.01035(48)	−0.00664(49)	0.00100(18)	0.060(21)	kHz
H_{KJ}	0.0665(16)	0.0468(25)	0.124(19)	0.414(60)	kHz
H_K	0.272(15)	1.412(76)	−0.0578(11)	9.8(10)	kHz
h_1	0.0231(85)	−0.0047(27)	0.0(fix)	0.0(fix)	Hz
h_2	−0.0318(28)	−0.0208(20)	−0.043(11)	−0.179(40)	Hz
h_3	−0.0143(12)	−0.0303(13)	0.0603(37)	−0.0335(83)	Hz
L_J	0.047(22)	−1.110(46)	−1.437(95)	22.5(91)	mHz
L_{62}	−0.00136(73)	−0.0100(17)	0.0138(32)	0.40(15)	Hz
L_{44}	0.0182(81)	0.0377(49)	0.574(56)	0.984(97)	Hz
L_{26}	0.0(fix)	0.031(25)	2.09(42)	10.1(20)	Hz
L_K	0.0(fix)	0.02396(88)	0.0(fix)	0.151(23)	kHz
ℓ_1	12.8(60)	0.0(fix)	0.0(fix)	0.0(fix)	μHz
ℓ_2	6.7(18)	0.0(fix)	0.0(fix)	0.0(fix)	μHz
ℓ_3	0.00223(83)	0.0233(14)	−0.3354(97)	0.0(fix)	mHz
ℓ_4	−0.92(57)	−3.17(57)	8.8(19)	0.0(fix)	μHz
S_J	0.0132(69)	−0.582(25)	0.0(fix)	32.2(141)	μHz
S_{82}	−0.00040(32)	−0.0107(18)	0.0(fix)	0.84(31)	mHz
S_{64}	−0.0157(57)	0.0(fix)	0.771(46)	0.0(fix)	mHz
S_{46}	−0.199(33)	0.197(28)	4.32(51)	14.3(14)	mHz
S_{28}	0.425(48)	−0.478(91)	12.1(33)	91.6(212)	mHz
S_K	0.0(fix)	0.0(fix)	0.0(fix)	0.0(fix)	mHz

parameters, however, show anomalous large changes upon vibrational excitation. This fact suggests that, although the barriers are high, the amplitudes of the torsional and inversional motions are large. As large amplitude motions enhance the vibration–rotation interactions, the higher order centrifugal corrections are required for fitting the data with an effective Hamiltonian for a given state.

On the basis of the spectroscopic parameters listed in Table 2, the rotational line positions can be predicted for a wide frequency range up to 2 THz for the ground state, and up to 1 THz for the excited vibrational states. A radio-astronomical survey of this molecule is now possible with highly reliable predictions.

Acknowledgements

The work in Cologne was supported in part by the Deutsche Forschungsgemeinschaft via grant SFB 301 and by special funding from the Science Ministry of the Land Nordrhein-Westfalen. The work in Lille was supported by CNRS (Programme National “Physico-chimie des Molecules interstellaires”) and the European Programme Human Capital and Mobility (Contract ERBCHRXCT 93-0157). In conjunction with the latter fund, the PECO Programme (ERBCIPDCT94-0614) financed the contribution from Poznan. I.M. is a Domestic Research Fellow of Japan Science and Technology Corporation.

References

- [1] S. Tsunekawa, J. Phys. Soc. Jpn. 33 (1972) 167.
- [2] D. Luckhaus, J. Chem. Phys. 106 (1997) 8409.
- [3] B. Hanoune, I. Morino, K. Kawaguchi, J. Mol. Spectrosc. 174 (1995) 172.
- [4] J. Makarewicz, M. Kreglewski, M.L. Senant, J. Mol. Spectrosc. 186 (1997) 162.
- [5] G. Taubmann, H. Jones, J. Mol. Spectrosc. 123 (1987) 366.
- [6] I. Morino, M. Fabian, H. Takeo, K.M.T. Yamada, J. Mol. Spectrosc. 185 (1997) 142.
- [7] G. Winnewisser, Vibrational Spectrosc. 8 (1995) 241.
- [8] I. Merke, L. Poteau, G. Wlodarczak, A. Bouddou, J. Demaison, J. Mol. Spectrosc. 177 (1996) 232.
- [9] D. Boucher, R. Bocquet, J. Burie, W. Chen, J. Phys. III (Paris) 4 (1994) 1467.
- [10] R.E. Nightingale, E.L. Wagner, J. Am. Chem. Soc. 75 (1953) 4092.
- [11] J.K.G. Watson, in: J. Durig (Ed.), Vibrational Spectra and Structure, 6, Elsevier, Amsterdam, 1977 chap. 1.
- [12] K.M.T. Yamada, S. Klee, J. Mol. Spectrosc. 166 (1994) 395.
- [13] K.M.T. Yamada, J. Mol. Spectrosc. 156 (1992) 512.