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Fourier transform microwave spectroscopy of *N*,*N*-dimethylacetamide

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Abstract

The jet-cooled Fourier-transform microwave spectrum of *N*,*N*-dimethylacetamide was recorded in the region of 12–24 GHz, and was analyzed to determine rotational constants and nuclear quadrupole coupling constants. Coriolis-like coupling parameters characterizing interaction between internal rotation of methyl groups and the overall rotation were also determined from internal-rotation tunneling splittings of the rotational transitions. The Coriolis-like coupling parameters permitted determination of the barrier heights to internal rotation of the three methyl groups, which were found to be 677, 237, and 183 cm^{-1} for the *C*-methyl top, the *trans*-*N*-methyl top and the *cis*-*N*-methyl top, respectively.

Keywords: *N*,*N*-dimethylacetamide; Fourier-transform microwave spectroscopy; Three non-equivalent methyl tops; Barrier heights to internal rotation

1. Introduction

N,*N*-Dimethylacetamide, CH_3—C(=O)—$N(CH_3)_2$, is a molecule of spectroscopic interest, because it contains three non-equivalent methyl tops. It is also of chemical importance because it contains a —C(=O)—N— group, which is related to a peptide molecule, such as *N*-methylacetamide [CH_3—C(=O)—NH—CH_3], in which a hydrogen atom is replaced by a methyl group. Recently, the nozzle-jet Fourier transform microwave spectrum of *trans*-*N*-methylacetamide was studied by Ohashi et al. [1], who determined barrier heights to internal rotation of the two methyl groups to be $V_3 = 79.06(9)\ cm^{-1}$ for the *N*-methyl top and $V_3 = 73.47(5)\ cm^{-1}$ for the *C*-methyl top. The main interest of the present study of *N*,*N*-dimethylacetamide is to determine how different the barrier heights for methyl top rotation are for these two molecules having a similar skeleton.

A number of properties of *N*,*N*-dimethylacetamide, including structures, vibrational frequencies, NMR chemical shift etc., have been computed in ab initio studies [2–5]. Internal rotation about the amide C–N bond of *N*,*N*-dimethylacetamide was investigated also in ab initio studies [2,3], but no literature treating internal rotation of the methyl groups were found. In the present microwave study, internal rotation of the methyl groups is treated by a detailed spectral analysis based on a group theoretical formalism, and information on barrier heights to the three methyl tops internal rotations is obtained.

2. Experimental

The Fourier-transform microwave (FTMW) spectrum of *N*,*N*-dimethylacetamide was measured in selected ranges between 12 and 24 GHz using the nozzle-jet FTMW spectrometer recently installed at Kanazawa University [6]. A reservoir nozzle was heated to about 70 °C to increase the sample concentration in the molecular beam. The carrier gas was an 80%/20% mixture of argon and helium. A commercial sample of *N*,*N*-dimethylacetamide was used without further purification. The spectral ranges to be measured were selected by referring to transition frequencies predicted from structural parameters obtained in an ab initio study [2].

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3. Tunneling-rotational Hamiltonian matrix based on a group theoretical treatment

The permutation-inversion (PI) group for *N*,*N*-dimethylacetamide is G_{54}, if one assumes that internal rotation is feasible for all three methyl groups, and that the heavy atom skeleton is planar. Elements of the PI group G_{54} are shown in Table 1. Table 2 gives the character table for this G_{54} group. In Fig. 1, a schematic tunneling splitting pattern of the $J = K = 0$ level is shown. Since the observed tunneling splittings are on the whole small, it seems appropriate to analyze the spectrum by a group theoretical treatment which is useful for the high barrier case. We describe below briefly the present treatment of the tunneling-rotational problem of *N*,*N*-dimethylacetamide, following the group theoretical method developed for the hydrazine molecule by Hougen [7].

Table 1
Elements of group G_{54} for *N*,*N*-dimethylacetamide[a]

O_1	E
O_2	(123)
O_3	(132)
O_4	(456)
O_5	(465)
O_6	(789)
O_7	(798)
O_8	(123)(456)
O_9	(123)(465)
O_{10}	(132)(456)
O_{11}	(132)(465)
O_{12}	(123)(789)
O_{13}	(123)(798)
O_{14}	(132)(789)
O_{15}	(132)(798)
O_{16}	(456)(789)
O_{17}	(456)(798)
O_{18}	(465)(789)
O_{19}	(465)(798)
O_{20}	(123)(456)(789)
O_{21}	(123)(456)(798)
O_{22}	(123)(465)(789)
O_{23}	(123)(465)(798)
O_{24}	(132)(456)(789)
O_{25}	(132)(456)(798)
O_{26}	(132)(465)(789)
O_{27}	(132)(465)(798)
O_{28}	(23)(56)(89)*
O_{29}	(123) O_{28}
O_{30}	(132) O_{28}
O_{31}	(456) O_{28}
O_{32}	(465) O_{28}
O_{33}	(789) O_{28}
O_{34}	(798) O_{28}
O_{35}	(123)(456) O_{28}
O_{36}	(123)(465) O_{28}
O_{37}	(132)(456) O_{28}
O_{38}	(132)(465) O_{28}
O_{39}	(123)(789) O_{28}
O_{40}	(123)(798) O_{28}
O_{41}	(132)(789) O_{28}
O_{42}	(132)(798) O_{28}
O_{43}	(456)(789) O_{28}
O_{44}	(456)(798) O_{28}
O_{45}	(465)(789) O_{28}
O_{46}	(465)(798) O_{28}
O_{47}	(123)(456)(789) O_{28}
O_{48}	(123)(456)(798) O_{28}
O_{49}	(123)(465)(789) O_{28}
O_{50}	(123)(465)(798) O_{28}
O_{51}	(132)(456)(789) O_{28}
O_{52}	(132)(456)(798) O_{28}
O_{53}	(132)(465)(789) O_{28}
O_{54}	(132)(465)(798) O_{28}

[a] 1, 2, 3, 4, 5, 6, 7, 8, and 9 denote hydrogen atoms in the three methyl groups.
* represents an inversion operation in the PI group theory.

The phenomenological Hamiltonian used here is written as follows:

$$H = h_v + AJ_z^2 + BJ_x^2 + CJ_y^2 - \Delta_J \mathbf{J}^4 - \Delta_{JK}\mathbf{J}^2 J_z^2 - \Delta_K J_z^4 - \delta_J 2\mathbf{J}^2\left(J_x^2 - J_y^2\right) - \delta_K\left[J_z^2\left(J_x^2 - J_y^2\right) + \left(J_x^2 - J_y^2\right)J_z^2\right] + iqJ_z + isJ_x. \quad (1)$$

The last two terms in Eq. (1) represent the Coriolis interaction between the overall rotation and the methyl internal rotation. Coefficients h_v, A, B, C, Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are of A_1 symmetry species, and q and s belong to A_2 symmetry species. The following transformation properties of the coefficients under the combined operation (‡) of Hermitian conjugation and time reversal are also useful:

$$h^{\ddagger} = +h \text{ for } h = h_v,\ A,\ B,\ C,\ \Delta_J,\ \Delta_{JK},\ \Delta_K,\ \delta_J, \text{ and } \delta_K$$
$$h^{\ddagger} = -h \text{ for } h = q \text{ and } s. \quad (2)$$

The 27 vibrational framework functions $|n\rangle$ $(n = 1, 2, \ldots, 27)$ appearing in the present treatment are represented by

$$|n\rangle = \mathrm{O}_n|1\rangle, \quad n = 1, 2, \ldots, 27, \quad (3)$$

where O_n's denote the PI operations as defined in Table 1. Based on the description given above, parameterized expressions for the tunneling-rotational Hamiltonian matrix elements are given as

$$\begin{aligned}\langle \Gamma; J, K|H|\Gamma; J, K'\rangle &= \sum_n f(\Gamma)_n[\langle 1|h_v|n\rangle\delta_{KK'} + \langle 1|A|n\rangle K^2\delta_{KK'} \\ &+ \langle 1|B|n\rangle\langle J, K|J_x^2|J, K'\rangle + \langle 1|C|n\rangle\langle J, K|J_y^2|J, K'\rangle \\ &- \langle 1|\Delta_J|n\rangle J^2(J+1)^2\delta_{KK'} - \langle 1|\Delta_{JK}|n\rangle J(J+1)K^2\delta_{KK'} \\ &- \langle 1|\Delta_K|n\rangle K^4\delta_{KK'} - 2\langle 1|\delta_J|n\rangle J(J+1)\langle J, K|(J_x^2 - J_y^2)|J, K'\rangle \\ &- \langle 1|\delta_K|n\rangle(K^2 + K'^2)\langle J, K|(J_x^2 - J_y^2)|J, K'\rangle] \\ &+ \sum_n \sqrt{3}g(\Gamma)_n[\langle 1|q|n\rangle K\delta_{KK'} + \langle 1|s|n\rangle\langle J, K|J_x|J, K'\rangle], \end{aligned} \quad (4)$$

where $f(\Gamma)_n$ and $g(\Gamma)_n$ are numerical factors given in Tables 3 and 4. In Tables 3 and 4, A_1 and A_2 species are both found in the AAA row, since A_1 and A_2 merely