Flexible ab initio geometry of methylamine and its internal rotation

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Abstract

A flexible geometry for the methylamine molecule was computed by the Becke–Perdew (B–P86) density functional method. Fifteen geometrical parameters (bonds and angles) were used for describing the flexible geometry. The reliability attained by the geometry was tested by the reproduction of four experimental rotation coefficients. © 1997 Elsevier Science B.V.

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1. Introduction

Methylamine is a totally flexible molecule with two different types of large amplitude motion, internal rotation and inversion, whose geometrical parameters (bonds and angles) depend on the large amplitude coordinates. It is not possible to determine the flexible geometry directly from the high resolution spectrum. From high resolution transitions, however, very accurate rotational coefficients can be obtained.

Recently we computed the flexible geometry of methylamine by different high level ab initio methods at a fixed internal rotation angle ($\alpha = 0$) and at different inversion coordinate values between $-130°$ and $+130°$ for amino wagging angles [1]. For the present investigation we have used the Becke–Perdew (B–P86) density functional method [2,3] with the 6-311G(d) basis set and have extended the calculation to the full range of α. To test the reliability of the geometry obtained, the inversion–internal rotation

averages of four rotational coefficients, computed from the flexible geometrical parameters, were compared with the experimental ones.

2. Results and discussion

Inversion and internal rotation are described by means of two curvilinear coordinates, τ and α [1]. The flexible geometry of the molecule can be described by 15 independent geometrical parameters. The geometrical parameter functions obtained from the computation are generally not of purely quadratic form, as was supposed in Ref. [4]. Furthermore, the calculation yielded different values for the CH parameters. This is in contrast with the usual assumption that the methyl group has a local threefold symmetry. According to this, even the 120° periodicity assumed for the internal rotation is not perfectly valid.

The rotational coefficients obtained from high resolution spectra are the averages of the inversion and the internal rotation [5]. Four coefficients determined

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from high resolution MW [6–8], MMW [9] and FIR [6,8] transitions are available. The first and second coefficients are R_J in terms of $J(J + 1)$ and R_K in terms of K^2 of the diagonal elements of the Hamiltonian. The third and fourth coefficients are Δ_{as} in the $k,k + 2$ off-diagonal elements and d_t in the $k, k + 1$ off-diagonal elements of the Hamiltonian. To connect the rotational coefficients and elements of the five-dimensional inertial tensor of the molecule we have used an extended form of the internal axis method (IAM). Since, in the case of the flexible methyl group, the internal rotation axis is undefined, we defined the tilt angle of the internal rotation axis relative to the CN bond by an empirical expression

$$\chi(\alpha, \tau) = \{\chi_0 - \chi_1(1 - \cos3\alpha)\}\sin\tau,$$

in which the constants were determined from the ground state and the first excited state values of the coefficient of d_t; d_t is extremely sensitive to the tilt angle.

According to Liu and Quade [10] the rotational coefficients are expanded in a Fourier series. For example, for the coefficient R_J the form of the expansion is

$$R_J(\alpha, \tau) = R_{J,0}(\tau) + \sum_{m=1}^{\infty} R_{J,m}(\tau)\cos(3m\alpha). \qquad (1)$$

Applying the expansion to the kinetic energy, the zero-order Hamilton operator is

$$\hat{H}_{ir}^0 = \frac{1}{2}\mu_{\alpha\alpha,0}(\tau)\hat{J}_\alpha^2 + \frac{1}{2}V_3(1 - \cos3\alpha),$$

where $\mu_{\alpha\alpha}^0(\tau)$ is the reduced inertial momentum of internal rotation, and

$$\hat{J}_\alpha = -i\frac{\partial}{\partial\alpha} + \rho k.$$

In the operator above, ρ is a periodicity parameter corresponding to the k dependence of the energy levels of internal rotation.

The effective potential function of inversion $V(\tau)$ was approximated by a function proposed by Coon et al. [11]. From Ref. [5], V_0 is 2081 cm^{-1} and τ_e is 53.86°. The shape parameter rh was fitted to the ν_0 value of the transition $n = 1 \leftarrow 0$ (ν_0 = 780.00 cm^{-1}). The reduced inertia momentum $\mu_{\tau\tau}(\tau)$ in the Hamilton operator of inversion [5] can also be calculated from the flexible geometry. The eigenfunctions for the inversion averaging can be computed by a numerical integration technique. After determining the average of the $\mu_{\alpha\alpha}^0(\tau)$ reduced momentum it is possible to calculate the eigensystem of the zero-order internal rotation Hamilton operator.

The α-dependent part of the reduced internal

Table 1
(a) Reproduction of the Ohashi–Hougen coefficients

	Obs. [9]	Calc.	Calc.[a]
$2h_{30}$ (MHz)	− 4987.4(1)	− 4987.42	− 4987.40
$2h_{50}$ (MHz)	5.68(4)	5.80	5.80
$2h_{70}$ (MHz)	0.00	− 0.01	− 0.01
$2h_{11}$ (cm^{-1})	264.5834(2)	264.583 38	264.583 37
$2h_{31}$ (MHz)	120 270.0(5)	120 269.96	120 270.03
$2h_{51}$ (MHz)	2680.6(3)	2681.52	2680.35
$2h_{71}$ (MHz)	100.1(3)	102.08	101.97

[a] Computed with fitted vibration–rotation correction coefficients.

(b) Parameters used at the reproduction of the Ohashi–Hougen coefficients

	Param.	Param.[a]
V_3 (cm^{-1})	682.9310	683.5695
V_6 (MHz)	110 819	117 924
V_9 (MHz)	− 104 026	− 135 144
V_{12} (MHz)	− 18 162	− 41 325
c_4 (MHz)	− 397.54	− 294.32
c_6 (MHz)	− 11.769	− 15.034
c_8 (MHz)	0.0933	− 0.0245

[a] Determined with fitted vibration–rotation correction coefficients.

Table 2
Rotational coefficients computed from the flexible geometry

	Obs. [9]	Calc.[a]	Obs.-Calc.[a]	Calc.[b]
R_J (MHz)	22 169.39	22 148.21	21.18	22 169.04
R_K (MHz)	80 986.40	80 615.90	370.50	80 986.39
Δ_{as} (MHz)	460.51	436.95	23.56	460.25
d_t (MHz)	0.00	0.00	0.00	0.00
d_t (MHz)[c]	100.00	100.34	-0.34	99.98

[a] $I_{xx}^{cor}=-0.08580$, $I_{zz}^{cor}=-0.09680$, $I_{zz}^{cor}=-0.03560$ and $I_{yz}^{cor}=0.02580$, computed at the equilibrium configuration, $\chi_0 = 2.45967°$ and $\chi_1 = 1.33202°$.

[b] $I_{xx}^{cor}=-0.12940$, $I_{yy}^{cor}=-0.09597$, $I_{yy}^{cor}=-0.05354$ and $I_{yz}^{cor}=0.03859$, $\chi_0 = 2.44655°$ and $\chi_1 = 1.34138°$.

[c] $v = 1$.

rotation momentum yields an important higher order contribution to the energy levels:

$$E_{ir}' = \frac{1}{2} \sum_{m=1}^{\infty} \langle \mu_{\alpha\alpha,m}(\tau)\rangle(\hat{J}_\alpha^2 \cos 3m\alpha + \cos 3m\alpha \hat{J}_\alpha^2).$$

There are other higher order contribution terms. The terms in the potential energy are

$$E_{pot}' = \frac{1}{2} \sum_{m=2}^{\infty} V_{3m}(1 - \langle \cos 3m\alpha \rangle)$$

and the terms from the kinetic energy are

$$E_{kin}' = \sum_{n=2}^{\infty} c_{2n}\langle \hat{J}_\alpha^{2n} \rangle.$$

There are higher order $E_{kin,pot}'$ mixed terms too.

The energy levels of the internal rotor and all quantum mechanical averages in the contribution have a periodic k dependence. Thus both the averages and the energy can be expanded in Fourier series. For example, the form of the expansion of the averages $\langle \cos 3m\alpha \rangle$ is

$$\langle \cos 3m\alpha \rangle = a_{m,0}^v + \sum_{j=1}^{\infty} a_{m,j}^v \cos\left[\frac{2\pi}{3}j(\rho k + \sigma)\right], \qquad (2)$$

where v is the torsional quantum number and σ is the torsional sublevel one ($\sigma = 0$, ± 1).

Comparing the Fourier expansion coefficients of the levels $E_{ir}^0 + E_{pot}' + E_{kin}' + E_{kin,pot}'$ with the $2h_{mv}$ Ohashi–Hougen expansion coefficients determined from the ground state ($v = 0$) [6,9] and the first internal rotation state ($v = 1$) [8,9] transitions, the constant V_3 and the full potential function of internal rotation can be determined. The results are summarized in Table 1. Having a well determined potential constant V_3, it is possible to compute the quantum mechanical averages and the expansion coefficients.

Substituting the expansion coefficients $a_{m,0}^v$ from eqn (2) into eqn (1), the average value of the corresponding rotational coefficient can be obtained. The results of the averaging are collected in Table 2. The inertial tensor elements were modified by correction terms arising from the vibration–rotation interaction. Unfortunately, the usual method described for rigid molecules [12] proved to be inapplicable to the problem of methylamine. The best result can be obtained if the linear and quadratic vibration–rotation interaction terms [12] are completed by the Coriolis term proposed by Iijima [13]. The second column of Table 2 contains the average values computed with the corrections mentioned above. To obtain information about the real order of the correction values, the calculation was also carried out with fitted corrections. The results are collected in the fourth column. It seems that the flexible geometry computed by the B–P86 method is a reliable one.

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