Accurate determination of an equilibrium structure in the presence of a small coordinate: The case of dimethylsulfide

J. Demaison [a,*], L. Margulès [a], H.D. Rudolph [b]

[a] Laboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France
[b] Department of Chemistry, University of Ulm, 89069 Ulm, Germany

ARTICLE INFO

ABSTRACT

The ab initio structure of dimethylsulfide is calculated at the CCSD(T) level of theory using a basis set of quadruple-ζ quality which takes into account the core correlation. The quadratic, cubic and semi-diagonal quartic force field of dimethylsulfide is calculated at the MP2 level of theory employing a basis set of triple-ζ quality. A semi-experimental equilibrium structure is derived from experimental ground-state rotational constants and rovibrational interaction parameters calculated from the ab initio force field. In spite of a very large number of isotopologues, the position of the in-plane hydrogens is poorly defined. This is explained by the small b-coordinate of these atoms. The problem is solved using the merged least-squares method where the input data are the semi-experimental and the ab initio structures.

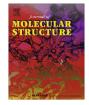© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The experimental determination of the equilibrium structure of a large molecule (more than four or five atoms) is an almost insuperable task because it requires the careful analysis of at least all fundamentally excited vibrational states of several isotopologues [1]. In theory, the mass-dependent r_m methods [2] are much easier to use because they only require the ground-state rotational constants. However, these methods necessitate the determination of several parameters in addition to the structural parameters. For this reason, the system of normal equations is usually ill-conditioned and the derived parameters are not accurate (except of course for very small molecules).

On the other hand, the semi-experimental equilibrium structure is rather easy to derive from the experimental ground-state rotational constants and the rotation–vibration interaction parameters (α-constants) calculated from an ab initio anharmonic force field [3]. Indeed, the semi-experimental equilibrium structure of several rather large molecules as glycine [4], proline [5], and alanine [6] have already been obtained. This method is generally considered to be the best means to obtain an accurate structure [3]. It normally delivers structures which are more accurate than the ab initio geometries because it is less sensitive to the problems of convergence of the basis set and of the method [7]. This is particularly true when the molecule contains electronegative or heavy (second row or higher) atoms.

However, although it is almost always possible to determine a structure from a least-squares fit to the moments of inertia, the result may be highly inaccurate. This happens in particular when there is a high correlation between some parameters which is encountered when there is no isotopic substitution available for one atom or when one atom is close to a principal inertial axis (small coordinate). In these cases, the semi-experimental method may fail to deliver an accurate structure. An interesting example is dimethylsulfide (DMS), $(CH_3)_2S$, where the H_s (in-plane hydrogen) atom is extremely close to the b-principal axis. This induces a very high correlation between the bond length $r(CH_s)$ and the bond angle $\angle(SCH_s)$.

DMS is also interesting for another reason. The two methyl groups are internal rotors which give rise to a sizable internal rotation splitting. A priori, it is not obvious that the methyl torsion can be treated as a small amplitude vibration when calculating the α-constants. The rotational spectrum of DMS has already been extensively investigated first by Rudolph et al. [8] and by Hayashi et al. [9,10]. The molecular g-factor was determined for $(CH_3)_2S$ and $(CD_3)_2S$ [11]. The quartic centrifugal distortion constants of these two isotopologues were also obtained [12,13]. The internal rotation splittings were analyzed several times [14–16]. The ground-state rotational constants of many isotopologues were

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determined [17] including the ^{33}S species [18], and the empirical substitution (r_s) structure was calculated several times, see Table 1. Finally, it is worth noting that the isolated CH stretching frequencies have been obtained by McKean and McQuillan [19] which is a useful information to estimate the r_e(CH) bond lengths [20].

The present paper is organized as follows. Section 2 determines empirical structures from the ground-state rotational constants, in Section 3 the optimization of the *ab initio* structure is discussed, in Section 4, the calculation of the *ab initio* anharmonic force field is explained, and in Section 5 the semi-experimental equilibrium structure is derived.

2. Empirical structures, r_0, $r_m^{(1)}$ and $r_m^{(2)}$

Inspection of Table 1, which lists the previous determinations of the r_s structure of DMS shows that there is a difficulty with the determination of the CH$_s$ bond length. In all cases but one, this length was kept fixed to an assumed value and, in the remaining case, it was indirectly estimated from the first-moment equations. Furthermore, the $\angle$(SCH$_s$) bond angle shows large variations. It is important to analyze the origin of these difficulties. For this reason, empirical structures of DMS will be determined in a first step.

Many approximate methods have been developed to determine an empirical structure using only ground-state rotational constants. The most recent and perhaps most useful method was developed by Watson et al. [2]. This so-called mass-dependent (r_m) structure technique takes into account, at least approximately, the variation of the rovibrational correction upon isotopic substitution and allows the determination of structures close to the assumed equilibrium structure. In this approach the relation between the ground-state moments of inertia and the equilibrium ones is written as

$$I_g^0 = I_g^e + \varepsilon_g, \quad g = a, b, c, \tag{1}$$

where ε_g is the vibrational correction. When the ε_g are neglected, it gives the effective (r_0) structure. Watson et al. [2] have shown that it is possible to express ε_g approximately as a function of the moments of inertia,

$$\varepsilon_g = c_g \sqrt{I_g^e}, \quad g = a, b, c, \tag{2}$$

This gives the $r_m^{(1)}$ structure. When there are small coordinates, it is necessary to refine this expression as

$$\varepsilon_g = c_g \sqrt{I_g^e} + d_g \left[\frac{\prod_i m_i}{M} \right]^{1/(2N-2)}, \quad g = a, b, c, \tag{3}$$

where N is the number of atoms in the molecule, m_i is the mass of atom i, M is the total mass of the molecule, and c_g and d_g are altogether six empirical parameters to be determined together with

the structural parameters during the least-squares fit. This procedure defines the $r_m^{(2)}$ method.

For the C–H and C–D bonds it is, in principle, necessary to take into account the variation of the effective bond length upon deuteration, which is usually called the Laurie correction. In favorable cases, this correction amounts to a shrinkage of the CD bond of about 0.003 Å compared to the CH bond length but it does not significantly affect the other parameters. Finally, it has to be noted that Eqs. (2) and (3) are valid only when the rotation of the principal inertial axes with respect to the overall shape of the molecule upon isotopic substitution is small, which is the case for DMS.

The ground-state rotational constants of most isotopologues come from Ref. [17]. They were calculated from low-J transitions using the Principal Axis Method (PAM). They are, thus, expected to be usable for a structure determination [21] without any correction. The rotational constants of a few multiply substituted deuterated species determined in the same way some time ago in Ulm [22] were also used. The rotational constants of (CH$_3$)$_2$^{33}S have been redetermined with the PAM using the experimental frequencies of Ref. [18]. The constants of the 20 investigated isotopologues are listed in Table 2. They give us 60 independent data to determine seven independent structural parameters which seems to be very favorable at first sight.

Sophisticated conditioning diagnostics have been proposed by Belsley [23] which calculate the condition indices (singular values of the scaled design matrix divided by the largest singular value) and the variance-decomposition proportions for the variables involved in the fit. For the condition indices larger than about 30, the variables which have a variance-decomposition proportion larger than 0.5 are affected by a degrading collinearity or near-dependency (reducing the number of digits to be trusted, i.e. causing larger errors). The largest condition index is called the condition number. Table 3 gives, besides the structural parameters for the r_0, $r_m^{(1)}$ and $r_m^{(2)}$ fits, the condition number, the number of condition indices larger than 30 and the largest correlation coefficient.

In the particular case of the r_0 structure obtained from a non-weighted least-squares fit to the ground-state moments of inertia, a degrading collinearity is observed between the bond length r_0(CH$_s$) and the bond angle $\angle$(SCH$_s$). This is supported by a high correlation coefficient of -0.996 between the errors of the two variables. This extreme collinearity may be explained by the fact that the H$_s$ atom is quite close to the b-principal axis, b_{r_0}(H$_s$) $= -0.029$ Å [24]. The use of the – in principle – more sophisticated $r_m^{(1)}$ method ($b_{r_m^{(1)}}$(H$_s$) $= -0.070$ Å) does not improve the situation. The condition number increases to 660 (from 162 for the r_0 method), there are now three condition indices larger than 30 (instead of one), the correlation coefficient between r_0(CH$_s$) and $\angle$(SCH$_s$) remains large, and the standard deviation of the fit does not decrease much. Furthermore, the value for r_m(CH$_s$) is obviously much too large whereas $\angle$(SCH$_s$) is probably too small (due to the negative correlation coefficient). The $r_m^{(2)}$ method, which

Table 1
Previous substitution structures of dimethylsulfide (bond lengths in Å, angles in °).

Ref.	[8]	[9]	[10]	[13]	[38]	[17]
Year	1960	1960	1961	1981	1989	2003
r(CS)	1.809(5)	1.800(2)	1.802(2)	1.8023(15)	1.802(1)	1.801(1)
$\angle$(CSC)	98.97(30)	98.9(2)	98.87(17)	98.82(12)	98.80(15)	98.97(5)
r(CH$_s$)	1.083(10)[a]	1.098(4)[a]	1.091 fixed		1.090 fixed	1.083(3)[b]
$\angle$(SCH$_s$)			106.63		106.68(60)	108.12(37)
r(CH$_a$)			1.091(5)		1.090(2)	1.093(1)
$\angle$(SCH$_a$)			110.75		110.77(30)	110.70(3)
$\angle$(H$_a$CH$_a$)		109.13(33)			109.63(52)	109.33(7)
$\angle$(H$_a$CH$_s$)					109.43(58)	108.95(23)

[a] Methyl group assumed symmetric.
[b] Indirectly estimated from the first-moment equations.