AB INITIO STUDY OF THE ROTATIONAL-TORSIONAL SPECTRUM OF METHYL FORMATE

M. L. SENENT,¹ M. VILLA,² F. J. MELÉNDEZ,³ AND R. DOMÍNGUEZ-GÓMEZ⁴

Received 2004 August 31; accepted 2005 March 9

ABSTRACT

The molecular structure of methyl formate is determined from ab initio calculations. The molecule presents two conformers (cis and trans) with a 5.3 kcal mol⁻¹ difference in energy. In the most stable cis conformer, the carbonyl group eclipses the methyl group. The internal rotation barriers are $V_3(\text{cis}) = 368 \text{ cm}^{-1}$ and $V_3(\text{trans}) = 26 \text{ cm}^{-1}$ for the methyl group and $V^{\text{CO}} = 4826 \text{ cm}^{-1}$ for the CO group. The dependence of the spectroscopic parameters on the torsional motions is detailed. The rotational-torsional energy levels have been calculated variationally up to $J = 6$ using a flexible model depending on the two torsional modes. Far-infrared frequencies and intensities are determined at room temperature. The rotational parameters have been computed to be $A = 20,040.473 \text{ MHz}$, $B = 6974.140 \text{ MHz}$, $C = 5350.705 \text{ MHz}$, $D_J = -0.510 \text{ kHz}$, $D_{JK} = 1.566 \text{ kHz}$, and $D_K = -0.619 \text{ kHz}$; and $A = 20,040.492 \text{ MHz}$, $B = 6974.399 \text{ MHz}$, $C = 5350.851 \text{ MHz}$, $D_J = 2.070 \text{ kHz}$, $D_{JK} = 14.712 \text{ kHz}$, and $D_K = 5.898 \text{ kHz}$ at the symmetric and E components of the cis ground state, respectively. The corresponding values for *trans*-methyl formate are $A = 47,380.066 \text{ MHz}$, $B = 4738.781 \text{ MHz}$, and $C = 4430.339 \text{ MHz}$; and $A = 47,389.697 \text{ MHz}$, $B = 4737.751 \text{ MHz}$, and $C = 4429.607 \text{ MHz}$.

Subject headings: astrochemistry — molecular data

1. INTRODUCTION

Quantum mechanical calculations represent an efficient procedure for a better understanding of experimental problems and for predicting and confirming molecular properties. Hence, the fundamental purpose of two of our previous papers has been the interpretation of the vibrational and rotational spectra of two prebiotic species detected in the interstellar medium (ISM): acetic acid and glycolaldehyde (Senent 2001, 2004). Both molecules are isomers that obey the empirical formula $\text{C}_2\text{O}_2\text{H}_4$ and show non-rigid properties that make the interpretation of the low-frequency spectra difficult. The discovery of glycolaldehyde (Hollis et al. 2000), the simplest monosaccharide, has been followed with great interest, given its biological importance.

The set of $\text{C}_2\text{O}_2\text{H}_4$ isomers presents a third component of astrophysical interest, the methyl formate $\text{H}-\text{COOCH}_3$. Although it is not the most stable species of the set, it is the most abundant in the ISM and has been the first to be detected in emission toward Sgr B2 (Brown et al. 1975). It is generally accepted that most millimeter and submillimeter emission lines observed toward Orion arise from only three molecules: methyl formate, dimethyl ether, and methanol (Johansson et al. 1984; Sutton et al. 1985; Blake et al. 1988). All of them present at least a methyl group capable of internal rotation, which causes the splitting of the energy levels into nondegenerate (A) and degenerate (E or G) substates. Dimethyl ether and methanol have been objects of previous studies performed in our laboratory (Senent et al. 1995; Muñoz-Caro et al. 1997).

Given its astrophysical relevance, the study of methyl formate as an isolated molecule has attracted major attention. Many papers concerning the vibrational (Wilmschurst 1957; Fateley & Miller 1961; Susi & Zell 1963; Susi & Scherer 1969; Blom & Günthard 1981; Chao et al. 1986) and rotational spectra (Curl 1959; Bauder 1979; Demaison et al. 1983; Plummer et al. 1984, 1986, 1987; Nadgaran & Baker 1995; Oesterling et al. 1995, 1999; Karakawa et al. 2001; Ogata et al. 2004) have been published. The molecular structure has been investigated using ab initio methods (John & Radom 1977; Fausto & Teixeira-Dias 1987; Hansen et al. 2000; Rocha et al. 2002; Good & Francisco 2002; Francisco 2003) or electron diffraction techniques (Cradock & Rankin 1980). However, many aspects concerning the interpretation of the rotational spectra and formation at low pressures and temperatures in the ISM remain misinterpreted. For example, although it is generally accepted that methyl formate can be produced from the methanol formed in the ice of interstellar grains, detailed studies of the ion-molecule processes using experimental and theoretical methods are unable to account for the full number of spectral lines observed (Herbst & Roberts 2004). Recently, a complete experimental and theoretical gas-phase study of methyl formate formation has been published (Horn et al. 2004).

The assignments of methyl formate vibrational and rotational spectra have special difficulties given the splitting of the levels caused by the two internal rotations. The first assignment of the methyl formate vibrational spectrum was performed in 1957 (Wilmschurst 1957). In this case, the two torsional modes were neglected in the study. Later, Fateley & Miller (1961) located the torsional methyl group at 130 cm^{-1} . It is well known that the molecule presents two different conformers. From low-temperature Ar matrix infrared spectroscopy, the energy difference between stable geometries, ΔH , has been determined to be $4.750 \pm 0.190 \text{ kcal mol}^{-1}$, and some observed bands have been assigned to the unstable trans conformer (Blom & Günthard 1981). Fundamental frequencies from Chao et al. (1986) are collected in the BASEMOL database (Crovisier 2002).

Many aspects related to the assignments of the millimeter and submillimeter lines of methyl formate remain incomplete. For

¹ Departamento de Astrofísica Molecular e Infrarroja (DAMIR), Instituto de Estructura de la Materia, CSIC, Calle Serrano 121, 28006 Madrid, Spain; imts420@iem.cfmac.csic.es.

² Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Purísima y Michoacán, s/n, CP 09340 Mexico DF, Mexico.

³ Laboratorio de Química Teórica, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Edificio 140, Ciudad Universitaria, Puebla, Puebla-72570, Mexico.

⁴ Departamento de Ingeniería Civil, Cátedra de Química, E. U. I. T. Obras Públicas, Universidad Politécnica de Madrid, Calle Alfonso XIII, 3-5, 28014 Madrid, Spain.

example, more or less complex global fits of lines corresponding to the A and E components of the ground and first excited states lead to quite different spectroscopic parameters. This disagreement is related to the most important spectroscopic parameters, the rotational constants, which are directly related to the molecular structure. Although there is an acceptable agreement for the “out-of-plane” C constant, different authors provide quite different “in-plane” constants. For example, the values of A and B of Demaison et al. (1983; 19,983.055 and 6914.4198 MHz), Plummer et al. (1986; 19,980.3907 and 6913.6822 MHz), Nadgaran & Baker (1995; 19,983 and 6914.928 MHz), Oesterling et al. (1999; 17,522.36993 and 9323.547665 MHz), Karakawa et al. (2001; 19,141.92 and 9112.39 MHz), and Ogata et al. (2004; 19,120.151 and 9181.7185 MHz) are not consistent. The BASEMOL (Crovisier 2002) database collects the results of Oesterling et al. (1999), who have also analyzed the deuterated isotopic variety D—COOCH₃ (Oesterling et al. 1995). Ab initio calculations can be a complementary technique in the molecular structure determination and for understanding the experimental results.

To our knowledge, accurate ab initio data capable of clarifying the rotational observations are not available. The relative energies and structures of the conformers published in the earlier ab initio studies (John & Radom 1977; Fausto & Teixeira-Dias 1987) were determined with methods unsuitable for a rotational analysis. Recent high-level calculations are limited to the determination of the cis structure and the vertical excitations (Hansen et al. 2000; Rocha et al. 2002; Good & Francisco 2002; Francisco 2003).

Thus, the main object of this paper is to obtain as much information as possible concerning structure and spectroscopic properties that can be derived from ab initio calculations. We analyzed the spectra from a two-dimensional flexible model depending on the modes responsible for the nonrigidity of the molecule. The potential energy surface and the parameters of the Hamiltonian are determined from ab initio energies and geometries. A final fit using the rovibrational energy levels allows us to determine rotational parameters corresponding to the vibrational energies, which are comparable with those obtained experimentally. The model has been previously tested

FIG. 1.—Two conformers of methyl formate.

for acetic acid (Senent 2001) and glycolaldehyde (Senent 2004).

2. COMPUTATIONAL DETAILS

All the calculations have been performed with Gaussian 03 (Frisch et al. 2004). The methyl formate potential energy surface has been determined with MP4(SDTQ)/cc-pVQZ ab initio calculations. The geometries of all the conformations have been optimized at the MP2/cc-pVQZ level. Fundamental frequencies have been computed at the MP2/cc-pVTZ level with the algorithm implemented in Gaussian 03 (Frisch et al. 2004). The torsional levels have been calculated variationally using a flexible two-dimensional model depending on the two torsional angles. The kinetic energy parameters of the Hamiltonian have been computed with the code MATRIZG.f (Senent 1998a) from the optimized geometries. The program BIDIM.f, designed for the study of the ethanol far-infrared spectrum (Senent et al. 2000), and the subroutines constructed for the study of the overall rotation of acetic acid (Senent 2001) have been employed for the determination of rovibrational energy levels and rotational parameters. Integral elements for the top symmetric functions are defined in Senent (1998b).

3. THE MOLECULAR STRUCTURE OF METHYL FORMATE

Methyl formate shows two planar conformations, cis and trans, of minimum energy, for which structural parameters are shown in Table 1. The terms cis and trans refer to the relative positions of the carbonyl and methyl groups (see Fig. 1). Both conformers are planar.

In the most stable cis geometry, the carbonyl group eclipses the methyl group. The methyl group is rotated in order to minimize the electrostatic repulsion responsible for the energy difference between conformers.

Two large-amplitude vibrations cause the nonrigid properties of methyl formate: the methyl group torsion and the OC—OC central bond torsion. The corresponding coordinates are represented by the symbols θ and α , which can be identified with the H6C3O1C2 and O4C2O1C3 dihedral angles (see Fig. 1). Their values at the cis and trans conformers are (180°, 0°) and (0°, 180°), respectively. The central bond torsion produces the secondary minimum, for which the relative energy has been calculated to be 5.3 kcal mol⁻¹ with MP4(SDTQ)/cc-pVQZ. The electrostatic potential maps (see Fig. 2) allow us to understand the enthalpy difference between conformers, which is in good agreement with the experimental value of Blom & Günthard (1981; 4.8 kcal mol⁻¹) obtained from the IR bands in an Ar matrix. The cis → trans transformation is hindered by a barrier

TABLE 1
STRUCTURAL PARAMETERS OF METHYL FORMATE CONFORMERS

Parameter	Cis	Trans
C2O1	1.3370	1.3442
C3O1	1.4344	1.4255
O4C2	1.2035	1.1963
H5C2	1.0922	1.0100
H6C3	1.0817	1.0883
H7C3	1.0851	1.0845
H8C3	1.0851	1.0845
C3O1C2	114.0	117.1
O4C2O1	125.6	122.9
H5C2O1	109.2	112.9
H6C3O1	105.5	111.3
H7C3O1	110.3	108.5
H8C3O1	110.3	108.5
O4C2O1C3	0.0	180.0
H5C2O1O4	180.0	180.0
H6C3O1C2	180.0	0.0
H7C3O1H5	119.7	120.4
H8C3O1H5	-119.7	-120.4

NOTE.—Distances are in Å, and angles are in degrees.

FIG. 2.—Electrostatic potential maps of *cis*- and *trans*-methyl formate.

calculated to be $13.8 \text{ kcal mol}^{-1}$. The process occurs with a slight variation of the internuclear distances.

Table 2 shows some structural parameters of the two conformers, the barriers that hinder the internal rotations, and the most important spectroscopic properties calculated in the potential energy surface wells. The MP2/cc-pVQZ rotational constants have been determined to be 19,945.037, 7017.551, and 5364.780 MHz for *cis*-methyl formate and 48,356.903, 4702.403, and 4404.249 MHz for *trans*-methyl formate. For the *cis* form, the calculated dipole moment components with respect to the principal axis, $\mu_a = 1.7437 \text{ D}$ and $\mu_b = 0.9640 \text{ D}$, are in reasonable agreement with the experimental data (Bauder 1979; $\mu_a = 1.63 \text{ D}$ and $\mu_b = 0.68 \text{ D}$). The dipole moment depends strongly on the OC—OC torsional coordinate, which should show the largest intensities in far-infrared bands. The rotational constants of Table 2 are not comparable with the experimental results, which are measured in the levels, not in the potential holes.

In Table 2, approximate one-dimensional internal barriers are shown. They have been calculated to be $V_3(\text{cis}) = 368 \text{ cm}^{-1}$, $V_3(\text{trans}) = 26 \text{ cm}^{-1}$, and $V^{\text{CO}} = 4826 \text{ cm}^{-1}$ ($13.8 \text{ kcal mol}^{-1}$) from the curves in Figures 3 and 4. These figures show the one-dimensional potential energy surfaces calculated by fitting the relative electronic energies of a set of conformations where

TABLE 2
MOLECULAR PROPERTIES OF METHYL FORMATE CONFORMERS

Property	Cis	Trans
Symmetry	C_s	C_s
μ (D)	1.9924	4.7053
Kinetic Energy Parameters		
A_e (MHz)	19,945.0367	48,356.9026
B_e (MHz)	7017.5506	4702.4032
C_e (MHz)	5364.7803	4404.2494
κ	-0.77329	-0.98643
B_{11} (cm^{-1})	6.9948	7.1831
B_{22} (cm^{-1})	5.7788	2.8895
B_{12} (cm^{-1})	-2.7498	-0.4040
V' (cm^{-1})	0.3412	0.2200
Potential Energy Barriers (cm^{-1})		
CH ₃ Cis	CH ₃ Trans	C—O Cis $\rightarrow$ Trans
$V_3 = 368$	$V_3 = 26$	$V^{\text{CO}} = 4826$
$V_3^{\text{ZPVE}} = 422$	$V_3^{\text{ZPVE}} = 9$	$V^{\text{CO}}_{\text{ZPVE}} = 4790$

NOTE.—Calculated with MP4(SDTQ)/cc-pVQZ//MP2/cc-pVQZ.

FIG. 3.—One-dimensional potential energy surfaces $V_3(\theta)$ for *cis*- and *trans*-methyl formate.

$3N - 7$ internal coordinates have been optimized. Dashed lines represent the potentials calculated from the total electronic energies, and the solid potentials comprise the zero-point vibrational correction (ZPVE). With these corrections, the barriers are $V_3(\text{cis}) = 422 \text{ cm}^{-1}$, $V_3(\text{trans}) = 9 \text{ cm}^{-1}$, and $V^{\text{CO}} = 4790 \text{ cm}^{-1}$. For $V_3(\text{cis})$, some experimental results arising from the fitting of

FIG. 4.—One-dimensional potential energy surface $V(\alpha)$ of methyl formate.

the millimeter and submillimeter observed lines are available in Oesterling et al. (1999; 398.763 cm^{-1}), Karakawa et al. (2001; 399.145 cm^{-1}), and Ogata et al. (2004; 379.440 cm^{-1}). In this last paper, the term V_6 is also considered in the fitting.

4. THE ROVIBRATIONAL SPECTRUM OF METHYL FORMATE

4.1. Theoretical Aspects

The rotational-torsional energy levels are calculated variationally using the flexible model in two dimensions developed for the study of the far-infrared spectrum of acetic acid (Senent 2001). The Hamiltonian for $J = 0$ can be identified with the pure torsional operator,

$$\hat{H}_T = -\left(\frac{\partial}{\partial\theta}\right)B_{11}\left(\frac{\partial}{\partial\theta}\right) - \left(\frac{\partial}{\partial\theta}\right)B_{12}\left(\frac{\partial}{\partial\alpha}\right) - \left(\frac{\partial}{\partial\alpha}\right)B_{12}\left(\frac{\partial}{\partial\theta}\right) - \left(\frac{\partial}{\partial\alpha}\right)B_{22}\left(\frac{\partial}{\partial\alpha}\right) + V(\theta, \alpha) + V'(\theta, \alpha) + V^{\text{ZPVE}}(\theta, \alpha), \quad (1)$$

where V , V' , and V^{ZPVE} represent the potential energy surface, the pseudopotential, and the zero-point vibrational correction and B_{11} , B_{22} , and B_{12} are the methyl torsion, the central bond torsion, and the torsion-torsion interaction kinetic energy parameters. They are related to the vibrational elements g_{44} , g_{55} , and g_{45} of the G matrix.

For each molecular structure, the kinetic parameters can be determined with our own algorithm (Senent 1998a). As all the parameters of the Hamiltonian transform as the totally sym-

metric representation of the C_{3v} symmetry group, they can be described by A_1 double Fourier series. The torsional levels are calculated variationally using as a trial function a symmetry-adapted double Fourier series. The convergence requires at least a Hamiltonian matrix with dimensions of 434 (A_1), 433 (A_2), 867 (E_x), and 867 (E_y).

Once the matrix is diagonalized, the most arduous effort is that of the classification of the energy levels, given the proximity of the two modes and the small gaps between splittings (Senent 2004). For this purpose, four criteria are considered: (1) the symmetry; (2) the values of the probability integrals around the minima, which allow one to distinguish between cis and trans levels; (3) the expectation values of the one-dimensional operators in the torsional levels, which allow one to assign the levels to each torsional mode; and (4) the intensities of the infrared transitions, which permit one to construct sequences of the levels.

The large difference between the oscillator strengths for the two modes permits one to use the infrared intensities for the assignments. The intensities of the Q branches of the out-of-plane type C bands are calculated with

$$I = \frac{q}{3R^2 e^2 B} \omega (P_j - P_i) \langle \phi_i | \mu_c | \phi_j \rangle^2, \quad (2)$$

where i and j represent two connected states, R is the average radius of the rotor, $B = (B_{11} + B_{22})^{1/2}$, μ_c is the dipole moment component transforming as the A_2 representation, P_K represents the Boltzmann population, ω is the frequency, and q is the nuclear statistical weight. The selection rules are shown in the Appendix (Table A1). For methyl formate, the statistical weight ratio corresponding to the A and E , nondegenerate and two-degenerate, representations of the C_{3v} group is 1:1.

For $J > 0$, the ro-torsional Hamiltonian is written as the sum of the pure rotational Hamiltonian and the interaction operator, defined by

$$\hat{H}_R = \sum_{\lambda=1}^3 \sum_{\mu=1}^3 g_{\lambda\mu} P_\lambda P_\mu, \quad \lambda, \mu = x, y, z, \quad (3)$$

$$\hat{H}_{RT} = \frac{\hbar i}{2} \sum_{\lambda=1}^3 \left[2g_{\lambda 4}(\theta) P_\lambda \frac{\partial}{\partial\theta} - \left(\frac{\partial g_{\lambda 4}}{\partial\theta} \right) \frac{\partial}{\partial\lambda} + 2g_{\lambda 5}(\alpha) P_\lambda \frac{\partial}{\partial\alpha} \left(\frac{g_{\partial\lambda 5}}{\partial\alpha} \right) \frac{\partial}{\partial\lambda} \right], \quad (4)$$

where x , y , and z are the molecular Cartesian axes A , B , and C ; P_λ represents the angular momentum components; and $g_{\lambda\mu}$ and $g_{\lambda n}$ are the rotational and ro-torsional elements of the G matrix (Senent 1998a). Following the principle axis method (PAM), the g_{ij} elements for $ij = 11, 22, 33, 13, 14, 34, 15$, and 35 transform as A_1 , and those for $ij = 12, 23, 15$, and 25 transform as A_2 .

The rovibrational energy levels are calculated variationally. We use a contracted basis set to reduce the dimension of the Hamiltonian matrix, which factorizes in four boxes corresponding to the A_1 , the A_2 , and the E two-degenerate representations (see the Appendix; Table A2). The contracted basis set may be a product of solutions of the vibrational Hamiltonian and solutions of the symmetric top in Cartesian coordinates (Senent 2001). Finally, the rotational parameters for the levels are evaluated by

TABLE 3

RELATIVE ELECTRONIC ENERGIES (IN cm^{-1}) OF THE SELECTED CONFORMATION OF METHYL FORMATE

θ (deg)	α (deg)	E_R	A	B	C
0.....	0	367.8	20,613.7	6709.7	5228.5
	90	191.7	20,297.6	6844.4	5287.9
	180	0.0 ^a	19,945.0	7017.6	5364.8
30.....	0	1383.0	21,114.9	5201.5	6516.8
	90	1315.2	21,039.2	5213.4	6539.3
	180	1199.7	20,680.9	5279.7	6677.3
60.....	-90	1270.1	20,749.2	5267.7	6654.5
	0	3854.7	23,112.8	5091.7	5951.4
	90	3622.5	22,996.4	5115.0	5984.1
90.....	180	3576.0	22,740.4	5147.5	6038.0
	-90	3796.2	22,851.0	5123.8	6003.7
	0	5421.5	26,794.1	4996.5	5363.4
120.....	90	5117.1	26,653.1	5023.0	5395.4
	180	4822.1	26,238.6	5076.3	5460.0
	-90	5087.0	26,366.6	5051.0	5428.7
150.....	0	4432.5	33,406.1	4842.0	4935.7
	90	4375.3	33,127.6	4858.8	4957.6
	180	3978.5	32,894.4	4883.7	4991.7
180.....	-90	4017.9	33,216.7	4864.1	4965.3
	0	2617.5	43,100.4	4518.8	4761.1
	90	2716.4	42,445.3	4536.4	4787.8
	180	2501.5	42,108.5	4553.1	4809.2
	-90	2414.0	42,781.5	4533.8	4780.5
	0	1823.0	48,356.9	4404.2	4702.4
	90	1843.0	47,755.8	4418.8	4724.3
	180	1849.3	47,091.4	4436.3	4750.5

^a $E_{\min} = -228.804898$ a.u.

fitting the energies and the expectation values of the rotational Hamiltonian operators at the levels to

$$\begin{aligned}
E = & \langle \psi_i | H_{\text{ROT}} | \psi_i \rangle = \frac{1}{2}(B + C)J(J + 1) \\
& + [A - \frac{1}{2}(B + C)] \langle \psi_i | \hat{J}_z^2 | \psi_i \rangle - D_J [J(J + 1)]^2 \\
& - D_{JK} J(J + 1) \langle \psi_i | \hat{J}_z^2 | \psi_i \rangle - D_K \langle \psi_i | \hat{J}_z^4 | \psi_i \rangle \\
& + H_J [J(J + 1)]^3 + H_{JK} [J(J + 1)]^2 \langle \psi_i | \hat{J}_z^2 | \psi_i \rangle \\
& + H_{KJ} J(J + 1) \langle \psi_i | \hat{J}_z^4 | \psi_i \rangle + H_K \langle \psi_i | \hat{J}_z^6 | \psi_i \rangle \\
& + \frac{1}{4}(B - C) \langle \psi_i | \hat{J}_+^2 + \hat{J}_-^2 | \psi_i \rangle \\
& + \delta_J J(J + 1) \langle \psi_i | \hat{J}_+^2 + \hat{J}_-^2 | \psi_i \rangle + \delta_K \langle \psi_i | \hat{J}_+^4 + \hat{J}_-^4 | \psi_i \rangle \\
& + \phi_J [J(J + 1)]^2 \langle \psi_i | \hat{J}_+^2 + \hat{J}_-^2 | \psi_i \rangle \\
& + \phi_{JK} J(J + 1) \langle \psi_i | \hat{J}_+^4 + \hat{J}_-^4 | \psi_i \rangle + \phi_K \langle \psi_i | \hat{J}_+^6 + \hat{J}_-^6 | \psi_i \rangle. \quad (5)
\end{aligned}$$

4.2. The Far-Infrared Spectrum of Methyl Formate

The far-infrared transitions of methyl formate have been calculated by solving variationally the Hamiltonian of equation (1). The kinetic and potential parameters are determined using ab initio calculations on a set of selected conformations (see Table 3), for which geometries have been computed optimizing $3N - 8$ parameters. In Tables 4, 5, and 6, the harmonic and anharmonic frequencies, the torsional levels, and the frequencies and intensities of methyl formate are shown.

The frequencies of some isotopic varieties of methyl formate have been calculated from the MP2/cc-pVTZ force field (see Table 2). We initiate the study of methyl formate spectra from a harmonic analysis for three reasons: first, the harmonic fundamentals

TABLE 4
FUNDAMENTAL FREQUENCIES (IN cm^{-1}) OF SOME METHYL FORMATE ISOTOPES CALCULATED WITH MP2/cc-pVTZ

ASSIGNMENT	Cis				Trans		
	HCO ₂ CH ₃		HCO ₂ CD ₃	DCO ₂ CH ₃	HCO ₂ CH ₃	HCO ₂ CD ₃	DCO ₂ CH ₃
	Anharmonic	Experimental ^a	Harmonic	Harmonic	Harmonic	Harmonic	Harmonic
A_1							
COC def.	349	318	285	309	389	359	381
OCO def.	767	767	723	770	647	627	643
O-CH ₃ st.	938	924	907	912	1049	901	1006
CH ₃ rock.	1167	1166	723	1080	1140	1023	1070
C-O st.	1213	1207	1002	1192	1285	1109	1149
CH bend.	1380	1371	1093	1248	1423	1153	1280
CH ₃ s-def.	1446	1445	1134	1478	1500	1241	1493
CH ₃ d-def.	1480	1454	1250	1521	1538	1432	1537
C=O st.	1762	1754	1409	1766	1829	1828	1800
CH st.	3007	2943	1790	2311	3016	2208	2241
CH ₃ s-st.	2959	2969	2221	3101	3081	2355	3080
CH ₃ d-st.	3090	3045	2398	3229	3176	3016	3176
A_2							
CH ₃ tors.	140	130	108	147	18	14	18
C-O tors.	335	332	335	307	191	182	177
CH bend.	1032	1032	926	893	1041	919	881
CH ₃ rock.	1168	1168	1055	1192	1193	1041	1193
CH ₃ d-def.	1466	1443	1089	1508	1507	1088	1507
CH ₃ d-st.	3054	3012	2371	3193	3196	2373	3196
ZPVE.	13376	13240	11602	13078	13609	11435	12914

^a Chao et al. (1986).

TABLE 5
TORSIONAL ENERGY LEVELS (IN cm^{-1})

$v\ v'$	SYMMETRY	Cis				TRANS		
		2D	+ZPVE	Experimental ^a	1D	2D	+ZPVE	1D
0 0	A_1	0 ^b	0 ^c	...	0	0 ^d	0 ^e	0
	E	0	0	...	0	6.3	7.0	6.1
1 0	A_2	123.6	134.8	130	126.1	61.3	61.8	64.6
	E	122.8	134.3	...	125.1	29.6	20.8	31.4
2 0	A_1	219.9	242.8	...	225.4	65.6	63.0	66.6
	E	228.0	248.9	...	233.0	111.1	110.0	115.0
3 0	A_2	334.1	358.0	...	339.6	...	...	...
	E	293.7	322.4	...	300.8	...	...	...
4 0	A_1	349.6	378.8	...	356.8	...	...	...
	E	409.3	434.6	...	415.8	...	...	...
0 1	A_2	321.7	329.5	332	294.2	181.5	177.1	148.3
	E	321.9	330.3	...	...	187.1	184.9	...
0 2	A_1	634.8	648.4	...	581.1	...	...	...
	E	635.3	649.1	...	...	...	...	...
0 3	A_2	939.8	957.2	...	860.8	...	...	...
	E	940.4	958.0	...	...	...	...	...
1 1	A_1	440.8	457.4	...	...	...	...	...
	E	439.9	456.9	...	...	...	...	...
1 2	A_2	531.2	608.4	...	...	...	...	...
	E	540.8	564.5	...	...	...	...	...
2 1	A_2	749.8	770.0	...	...	...	...	...
	E	748.6	769.3	...	...	...	...	...

^a Chao et al. (1986).
^b 228.8 cm^{-1} .
^c 240.2 cm^{-1} .
^d 1924.8 cm^{-1} .
^e 1969.3 cm^{-1} .

represent preliminary frequencies; second, they allow one to distinguish the minima and the saddle points of the potential energy curves; and third, they allow one to predict the strength of the interactions among modes. The deuterated forms ensure the correct assignment. In the case of the most stable conformer,

anharmonic frequencies are also calculated using perturbation theory. For some medium- and small-amplitude modes, the agreement between anharmonic frequencies and experimental values is quite good. In all the cases, the accuracy is reasonable for the level of ab initio calculations that we have used. The anharmonic

TABLE 6
PREDICTED FAR-INFRARED FREQUENCIES (IN cm^{-1}) AND ABSOLUTE INTENSITIES FOR CIS AND TRANS METHYL FORMATE CALCULATED AT 273.15 K

$v_i v'_i \rightarrow v_j v'_j$	SYMMETRY	CIS			TRANS		
		Variational Frequency	Intensity	ν_{18} Perturbation Theory	Variational Frequency	Intensity	ω_{17}
CH ₃							
00 $\rightarrow$ 10	$A_1 \rightarrow A_2$	134.8	0.626×10^{-6}	140	61.8	0.928×10^{-10}	18
	$E \rightarrow E$	134.3	0.609×10^{-6}	...	20.8	0.031×10^{-10}	...
10 $\rightarrow$ 20	$A_2 \rightarrow A_1$	108.0	0.054×10^{-6}	87	...	...	...
	$E \rightarrow E$	114.5	0.089×10^{-6}	...	...	...	...
OC—OC							
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	329.5	0.0118	335	177.1	0.274×10^{-7}	191
	$E \rightarrow E$	330.3	0.0111	...	177.9	0.261×10^{-7}	...
01 $\rightarrow$ 02	$A_2 \rightarrow A_1$	318.9	0.0039	331	...	...	...
	$E \rightarrow E$	318.8	0.0039	...	...	...	...
02 $\rightarrow$ 03	$A_1 \rightarrow A_2$	308.8	0.0011	...	...	...	...
	$E \rightarrow E$	308.9	0.0011	...	...	...	...
10 $\rightarrow$ 11	$A_2 \rightarrow A_1$	322.6	0.0057	332	...	...	...
	$E \rightarrow E$	322.5	0.0057	...	...	...	...
01 $\rightarrow$ 11	$A_2 \rightarrow A_1$	127.9	0.074×10^{-7}	137	...	...	...
	$E \rightarrow E$	126.6	0.744×10^{-7}	...	...	...	...
11 $\rightarrow$ 21	$A_1 \rightarrow A_2$	151.0	0.727×10^{-7}	...	...	...	...
	$E \rightarrow E$	107.6	0.016×10^{-7}	...	...	...	...
11 $\rightarrow$ 12	$A_1 \rightarrow A_2$	312.6	0.0020	...	...	...	...
	$E \rightarrow E$	312.4	0.0020	...	...	...	...

FIG. 5.—Two-dimensional potential energy surface of methyl formate.

fundamentals of the two torsional modes have been determined to be 140 and 335 cm^{-1} for the *cis* form, and the harmonic fundamentals, to be 18 and 191 cm^{-1} for the *trans* form. Experimental *cis* values are 130 and 332 cm^{-1} . By regarding the energy and symmetry of the modes, one may expect the presence of Fermi interactions between the *cis* A_1 COC deformation mode (348 cm^{-1}) and the *cis* CH_3 torsion overtone ($140 \times 2 = 280 \text{ cm}^{-1}$), and between the *trans* A_1 COC deformation mode (389 cm^{-1}) and the *trans* central bond torsion overtone ($191 \times 2 = 382 \text{ cm}^{-1}$).

These torsional fundamentals represent a first approximation. The methods implemented in Gaussian 03 have been developed for semirigid molecules showing a single minimum. Nonrigid molecules show various minima separated by barriers that produce the splitting of the levels by tunnelling. For this reason, the determination of realistic torsional energies implies the consideration of all the minima. The potential energy surface is shown in Figure 5. It has been determined by fitting to a double Fourier series the MP4(SDTQ)/cc-pVQZ relative energies of the set of 26 conformations selected (see Table 3). Then,

$$\begin{aligned}
 V(\theta, \alpha) = & 2982.2 - 723.5 \cos(\alpha) - 2042.6 \cos(2\alpha) \\
 & - 112.4 \cos(3\alpha) + 80.6 \cos(4\alpha) + 10.0 \cos(5\alpha) \\
 & - 6.5 \cos(6\alpha) + 150.2 \cos(3\theta) + 28.0 \cos(3\theta) \cos(\alpha) \\
 & - 107.5 \cos(3\theta) \cos(\alpha) + 62.1 \cos(3\theta) \cos(3\alpha) \\
 & + 42.3 \cos(3\theta) \cos(4\alpha) + 8.5 \cos(3\theta) \cos(5\alpha) \\
 & + 0.4 \cos(3\theta) \cos(6\alpha) + 1.7 \cos(6\theta) \\
 & + 0.3 \cos(6\theta) \cos(\alpha) - 6.3 \cos(6\theta) \cos(2\alpha) \\
 & + 0.4 \cos(6\theta) \cos(3\alpha) + 1.4 \cos(6\theta) \cos(4\alpha) \\
 & - 1.0 \cos(6\theta) \cos(5\alpha) - 0.4 \cos(6\theta) \cos(6\alpha) \\
 & - 60.5 \sin(3\theta) \sin(\alpha) + 113.8 \sin(3\theta) \sin(2\alpha) \\
 & - 52.9 \sin(3\theta) \sin(3\alpha) - 39.5 \sin(3\theta) \sin(4\alpha) \\
 & - 7.5 \sin(3\theta) \sin(5\alpha).
 \end{aligned} \tag{6}$$

The surface has been corrected by adding the zero-point vibrational correction calculated within the harmonic approximation at the MP4(SDQ)/cc-pVQZ level.

In molecules with hindered internal rotation, the methyl groups lose the “static” C_{3v} symmetry, in spite of the fact that the “dynamic” symmetry is preserved. This “symmetry dilemma” is evidenced during the geometry optimization, if a single internal coordinate is frozen. For example, if the H6C3O1C2 dihedral angle is frozen at θ , the resulting energy is different from the one obtained by freezing H7C3O1C2 at $\theta + 120^\circ$, or by freezing H8C3O1C2 at $\theta - 120^\circ$. In previous papers (Villa et al. 1999; Szalay et al. 2002), we have proposed two possible ways of minimizing or eliminating the numerical errors derived from the dilemma. The first is to select a set of conformations where one of the dihedral angles is fixed at 0° , 180° , and 90° . Thus, one of the methyl CH bonds remains in the plane or perpendicular to the molecular plane. The second is to optimize the geometry by freezing the torsional coordinate defined as $\theta = 1/3(\theta_1 + \theta_2 + \theta_3)$. In this case, the remaining linear combinations of internal coordinates are allowed to be relaxed. In the case of applying this last solution in correlated calculations, it will be necessary to develop new ab initio software.

The torsional energy levels of Table 5 are classified using the four criteria described in the theoretical section of this paper. The calculations have been performed without considering the zero vibrational correction (2D) and including the zero-point vibrational correction (+ZPVE). As is well known, ZPVE is the most important correction in accurate calculations of vibrational levels in the case of reduced models. Nevertheless, the effect of the pseudopotential on the levels is negligible. The calculations have also been performed in one dimension (1D) using the potential energy surfaces presented in Figures 3 and 4. In principle, the one-dimensional results were considered for evaluating the interactions between the two torsions. They have been achieved neglecting the ZPVE corrections.

TABLE 7
ROTATIONAL LEVELS (IN cm^{-1}) FOR THE TWO COMPONENTS A AND E
OF THE CIS AND THE TRANS VIBRATIONAL GROUND STATES

$J_{ K_a K_c }$	CIS		TRANS	
	A	E	A	E
0 0 0 A_1	0.000	0.012	1729.111	1736.061
1 0 1 A_2	0.411	0.424	1729.417	1736.367
1 1 1 A_2	0.847	0.859	1730.840	1737.789
1 1 0 A_1	0.901	0.913	1730.850	1737.800
2 0 2 A_1	1.229	1.241	1730.029	1736.978
2 1 2 A_1	1.615	1.627	1731.441	1738.391
2 1 1 A_2	1.778	1.790	1731.472	1738.421
2 2 1 A_1	3.085	3.096	1735.739	1742.690
2 2 0 A_1	3.090	3.102	1735.739	1742.690
3 0 3 A_2	2.439	2.453	1730.946	1737.895
3 1 3 A_2	2.767	2.777	1732.343	1739.293
3 1 2 A_1	3.089	3.101	1732.405	1739.354
3 2 2 A_1	4.319	4.330	1736.656	1743.607
3 2 1 A_2	4.342	4.354	1736.656	1743.607
3 3 1 A_2	6.639	6.645	1743.794	1750.746
3 3 0 A_1	6.636	6.651	1734.794	1750.746

The one-dimensional model appears to be very inefficient for the central bond torsion. For the methyl torsion, a displacement of $\sim 3\text{ cm}^{-1}$ up to the lower frequencies is observed when the one- and two-dimensional calculations are compared. The two-dimensional mode improves the calculations of the methyl band position. Furthermore, as was first observed for ethanol (Senent et al. 2000) and acetic acid (Senent 2001), the reduced model efficiency is always more evident on the higher frequency torsional mode.

The fundamental anharmonic frequencies of the methyl and central bond torsion of *cis*-methyl formate have been computed to be $123.6\text{ (}A\text{)}$ and $122.8\text{ cm}^{-1}\text{ (}E\text{)}$ and to be $321.7\text{ (}A\text{)}$ and $321.9\text{ cm}^{-1}\text{ (}E\text{)}$, without the ZPVE, and considering the ZPVE

they have been calculated at $134.8\text{ (}A\text{)}$ and $134.3\text{ cm}^{-1}\text{ (}E\text{)}$ and $329.5\text{ (}A\text{)}$ and $330.2\text{ cm}^{-1}\text{ (}E\text{)}$. These last calculations are in a very good agreement with the experimental values of $130\text{ (CH}_3\text{)}$ and $332\text{ cm}^{-1}\text{ (OC-OC)}$; Chao et al. 1986). The difference of $\sim 4\text{ cm}^{-1}$ between the calculated and experimental values for the methyl group can arise from the way that the symmetry dilemma has been corrected.

All the calculated trans levels lie over the methyl torsional barrier. The ground states have been localized at 1924.8 (without the ZPVE correction) and 1969.3 cm^{-1} (with the ZPVE correction). They show two components, A and E , separated by 6.3 and 7 cm^{-1} . The assignment of these levels is especially arduous and has been performed with the help of one-dimensional results. The methyl torsion anharmonic fundamental has been found to lie at 61.8 cm^{-1} , and the one for the central bond torsion at 177.1 cm^{-1} . The harmonic frequencies are 18 and 191 cm^{-1} (see Table 4).

The frequencies and intensities of the transitions connecting the lowest levels are shown in Table 6. As was expected, the transitions assigned to OC-OC are the strongest ones. The intensities are calculated at 273.15 K . At very low temperatures ($\sim 20\text{ K}$), only the ground state of the *cis* conformer is populated.

4.3. The Rotational Parameters of Methyl Formate

The rovibrational levels for $J > 0$ have been computed by solving variationally the Hamiltonian of equation (6). In Table 7, the rotational energies for the A and E substates of the *cis* and *trans* ground states are shown. By fitting to equation (5) the expectation values of the Watson Hamiltonian operators, the rotational parameters have been computed to be $A = 20,040.473\text{ MHz}$, $B = 6974.140\text{ MHz}$, $C = 5350.705\text{ MHz}$, $D_J = -0.510\text{ kHz}$, $D_{JK} = 1.566\text{ kHz}$, and $D_K = -0.619\text{ kHz}$; and $A = 20,040.492\text{ MHz}$, $B = 6974.399\text{ MHz}$, $C = 5350.851\text{ MHz}$, $D_J = 2.070\text{ kHz}$, $D_{JK} = 14.712\text{ kHz}$, and $D_K = 5.898\text{ kHz}$ at the symmetric and E components of the *cis* ground state,

TABLE 8
COMPUTED ROTATIONAL PARAMETERS OF *Cis*- AND *Trans*-METHYL FORMATE AT THE LOWEST TORSIONAL STATES

GROUND STATE Cis (0 0)	A		B	
	Calculated	Experimental ^a	Calculated	Experimental ^b
A (MHz).....	20,040.473	19,985.7623	20,040.492	19,980.3907
B (MHz).....	6974.140	6914.7577	6974.399	6913.6822
C (MHz).....	5350.851	5304.4681	5350.851	5304.5114
D_J (kHz).....	-0.510	6.1781	2.070	5.8895
D_{JK} (kHz).....	1.566	-17.1981	14.712	-23.313
D_K (kHz).....	-0.619	82.3578	5.898	75.4009
δ_J (kHz).....	-0.237	1.9502	-0.223	1.8571
δ_J (kHz).....	-0.309	7.6605	-1.554	2.057
EXCITED STATES	Cis (1 0)		TRANS (0 0)	
	A	E	A	E
A (MHz).....	20,164.023	20,167.381	47,380.066	47,389.645
B (MHz).....	6913.492	6911.891	4738.781	4737.653
C (MHz).....	5323.755	5323.043	4430.339	4429.715
D_J (kHz).....	-0.186	1.014	49.831	34.346
D_{JK} (kHz).....	2.087	-8.374	-252.397	-64.170
D_K (kHz).....	-0.197	18.119	363.661	54.583
δ_J (kHz).....	-0.499	1.542	-7.278	-47.373
δ_J (kHz).....	-0.577	2.961	-12.135	-21.751

^a Plummer et al. (1984).
^b Plummer et al. (1986).

respectively. The corresponding values for *trans*-methyl formate are $A = 47,380.066$ MHz, $B = 4738.781$ MHz, and $C = 4430.339$ MHz; and $A = 47,389.697$ MHz, $B = 4737.751$ MHz, and $C = 4429.607$ MHz (see Table 8).

As the parameters have been computed in the energy levels, they are comparable with experimental data, in the case of the *cis* form (Plummer et al. 1984, 1986). To our knowledge, there is no available experimental data for *trans*-methyl formate. For *cis*-methyl formate, various studies, which present important disagreements concerning the fitted parameters, are available. The discordances arise from the different fitting techniques and are not limited to the distortion constants. The effect concerns the in-plane A and B rotational constants, which are the most important parameters to characterize the molecular structure. Electrostatic interactions introduce in-plane molecular distortion that has an effect in the A/B ratio.

Our A and B parameters of 20,040.473 and 6974.140 MHz, respectively, are in good agreement with the earlier papers ($A/B = 19,985.7623/6914.7577$, Plummer et al. 1984; $A/B = 19,981.248/6914.02$, Nadgaran & Baker 1995). Recent data ($A/B = 17,522.36993/9323.547665$, Oesterling et al. 1999; $A/B = 19,120.151/9181.7185$, Ogata et al. 2004) are far away from the ab initio results. In these cases, a global fitting including

together the A and E components of the two states is performed using a large number of parameters.

By taking into consideration what is the usual accuracy of the Möller-Plesset ab initio calculations for like molecules (see, e.g., our results for two isomers of methyl formate: acetic acid [Senent 2001] and glycolaldehyde [Senent 2004]), it may be asserted that the global fits do not provide a real description of the molecular structure. The significance of the rotational parameters is not realistic. The problem can be related to the torsional dependence of the molecular geometry.

For a better understanding of the problem, we provide the values of the rotational constants for the selected conformations in Table 3. For example, in the *cis* form, the A parameter varies by 352 MHz when the energy changes 191.7 cm^{-1} . It is evident that the torsional dependence of the rotational constants is clearly important and has to be considered at the moment of the selection of the fitting parameters.

This work has been also supported by the Ministerio de Ciencia y Tecnología of Spain, grant AYA2002-02117, and the Consejo Nacional de Ciencia y Tecnología de México, grant n1 37075-E.

APPENDIX

TABLE A1
SELECTION RULES FOR THE INFRARED TRANSITIONS

A-Type Bands $\mu_a A_1$	B-Type Bands $\mu_b A_1$	C-Type Bands $\mu_c A_2$
$A_1 \leftrightarrow A_1$	$A_1 \leftrightarrow A_1$	$A_1 \leftrightarrow A_2$
$A_2 \leftrightarrow A_2$	$A_2 \leftrightarrow A_2$	$E_x \leftrightarrow E_y$
$E_x \leftrightarrow E_y$	$E_x \leftrightarrow E_x$	...

TABLE A2
ROTATIONAL TORSIONAL FUNCTIONS FOR METHYL FORMATE

Symmetry	Torsional Eigenfunctions	J	K
A_1	$\sum (A_i \cos 3n\theta \cos l\alpha + B_i \sin 3n\theta \sin l\alpha)$	Even	Even
	$\sum (A_i \cos 3n\theta \sin l\alpha + B_i \sin 3n\theta \cos l\alpha)$	Even	Odd
	$\sum (A_i \cos 3n\theta \cos l\alpha + B_i \sin 3n\theta \sin l\alpha)$	Odd	Odd
	$\sum (A_i \cos 3n\theta \sin l\alpha + B_i \sin 3n\theta \cos l\alpha)$	Odd	Even
A_2	$\sum (A_i \cos 3n\theta \cos l\alpha + B_i \sin 3n\theta \sin l\alpha)$	Even	Odd
	$\sum (A_i \cos 3n\theta \sin l\alpha + B_i \sin 3n\theta \cos l\alpha)$	Even	Even
	$\sum (A_i \cos 3n\theta \cos l\alpha + B_i \sin 3n\theta \sin l\alpha)$	Odd	Even
	$\sum (A_i \cos 3n\theta \sin l\alpha + B_i \sin 3n\theta \cos l\alpha)$	Odd	Odd
E_x	$\sum \{A_i \cos[(3n \pm 1)\theta] \cos l\alpha + B_i \sin[(3n \pm 1)\theta] \sin l\alpha\}$	Even	Even
	$\sum \{A_i \cos[(3n \pm 1)\theta] \sin l\alpha + B_i \sin[(3n \pm 1)\theta] \cos l\alpha\}$	Even	Odd
	$\sum \{A_i \cos[(3n \pm 1)\theta] \cos l\alpha + B_i \sin[(3n \pm 1)\theta] \sin l\alpha\}$	Odd	Odd
	$\sum \{A_i \cos[(3n \pm 1)\theta] \sin l\alpha + B_i \sin[(3n \pm 1)\theta] \cos l\alpha\}$	Odd	Even
E_y	$\sum \{A_i \cos[(3n \pm 1)\theta] \cos l\alpha + B_i \sin[(3n \pm 1)\theta] \sin l\alpha\}$	Even	Odd
	$\sum \{A_i \cos[(3n \pm 1)\theta] \sin l\alpha + B_i \sin[(3n \pm 1)\theta] \cos l\alpha\}$	Even	Even
	$\sum \{A_i \cos[(3n \pm 1)\theta] \cos l\alpha + B_i \sin[(3n \pm 1)\theta] \sin l\alpha\}$	Odd	Even
	$\sum \{A_i \cos[(3n \pm 1)\theta] \sin l\alpha + B_i \sin[(3n \pm 1)\theta] \cos l\alpha\}$	Odd	Odd

REFERENCES

- Bauder, A. 1979, J. Phys. Chem. Ref. Data, 8, 583
 Blake, G. A., Sutton, E. C., Masson, C., & Phillips, T. G. 1986, ApJS, 60, 357
 Blom, C. E., & Günthard, Hs. H. 1981, Chem. Phys. Lett., 84, 267
 Brown, R. D., Crofts, J. G., Gardner, F. F., Godfrey, P. D., Robinson, B. J., & Whiteoak, J. B. 1975, ApJ, 197, L29
 Chao, J., Hall, K. R., Marsh, K. N., & Wilhoit, R. C. 1986, J. Phys. Chem. Ref. Data, 15, 1369
 Craddock, S., & Rankin, D. W. H. 1980, J. Mol. Struct., 69, 145
 Crovisier, J. 2002, BASEMOLE (ver. 4.2; Meudon: Obs. Paris-Meudon), <http://www.usr.obspm.fr/~crovisie/basemole>
 Curl, R. F. 1959, J. Chem. Phys., 30, 1529
 Demaison, J., Boucher, D., Dubrulle, A., & Van Eijck, B. P. 1983, J. Mol. Spectrosc., 102, 260
 Fateley, W. G., & Miller, F. A. 1961, Spectrochim. Acta A, 17, 857

- Fausto, R., & Teixeira-Dias, J. J. C. 1987, *J. Mol. Struct. Theochem*, 150, 381
- Francisco, J. S. 2003, *J. Am. Chem. Soc.*, 125, 10475
- Frisch, M. J., et al. 2004, *Gaussian 03* (rev. C.02; Wallingford: Gaussian, Inc.)
- Good, D. A., & Francisco, J. S. 2002, *J. Phys. Chem. A*, 106, 1733
- Hansen, J. C., Li, Y., Francisco, J. S. Szente, J. J., & Matti Maricq, M. 2000, *J. Chem. Phys.*, 113, 6465
- Herbst, E., & Roberts, H., 2004, in 59th Int. Symp. on Molecular Spectroscopy (Columbus: Ohio State Univ.), WI09
- Hollis, J. M., Lovas, F. J., & Jewell, P. R. 2000, *ApJ*, 540, L107
- Horn, A., Mollendal, H., Sekiguchi, E., Uggerud, E., Roberts, H., Herbst, E., Viggiano, A. A., & Fridgen, T. D. 2004, *ApJ*, 611, 605
- Johansson, L. E. B., et al. 1984, *A&A*, 130, 227
- John, I. G., & Radom, L. 1977, *J. Mol. Struct.*, 36, 133
- Karakawa, Y., Oka, K., Odashima, H., Takagi, K., & Tsunekawa, S. 2001, *J. Mol. Spectrosc.*, 210, 196
- Muñoz-Caro, C., Niño, A., & Senent, M. L. 1997, *Chem. Phys. Lett.*, 273, 135
- Nadgaran, H., & Baker, J. G. 1995, in ASP Conf. Ser. 81, Workshop on Laboratory and Astronomical High-Resolution Spectra, ed. A. J. Sauval, R. Blomme, & N. Grevesse (San Francisco: ASP), 329
- Oesterling, L. C., Albert, S., De Lucia, F. C., Sastry, K. V. L. N., & Herbst, E. 1999, *ApJ*, 521, 255
- Oesterling, L. C., Ferguson, D. W., Herbst, E., & De Lucia, F. C. 1995, *J. Mol. Spectrosc.*, 172, 469
- Ogata, K., Odashima, H., Takagi, K., & Tsunekawa, S. 2004, *J. Mol. Spectrosc.*, 225, 14
- Plummer, G. M., Herbst, E., & De Lucia, F. C. 1987, *ApJ*, 318, 873
- Plummer, G. M., Herbst, E., De Lucia, F. C., & Blake, G. A. 1984, *ApJS*, 55, 633
- . 1986, *ApJS*, 60, 949
- Rocha, A. B., Pimentel, A. S., & Bielschowsky, C. E. 2002, *J. Phys. Chem. A*, 106, 181
- Senent, M. L. 1998a, *Chem. Phys. Lett.*, 296, 299
- . 1998b, *J. Mol. Spectrosc.*, 191, 265
- . 2001, *Mol. Phys.*, 15, 1311
- . 2004, *J. Phys. Chem. A*, 108, 6286
- Senent, M. L., Moule, D. C., & Smeyers, Y. G. 1995, *J. Chem. Phys.*, 102, 5952
- Senent, M. L., Smeyers, Y. G., Dominguez-Gómez, R., & Villa, M. 2000, *J. Chem. Phys.*, 112, 5809
- Susi, H., & Scherer, J. R. 1969, *Spectrochim. Acta A*, 25, 1243
- Susi, H., & Zell, T. 1963, *Spectrochim. Acta A*, 19, 1933
- Sutton, E. C., Blake, G. A., Masson, C., & Phillips, T. G. 1985, *ApJS*, 58, 341
- Szalay, V., Császár, A. G., & Senent, M. L. 2002, *J. Chem. Phys.*, 117, 6489
- Villa, M., Herrera, G., & Smeyers, Y. G. 1999, *Chem. Phys.*, 306, 72
- Wilmshurst, J. K. 1957, *J. Mol. Spectrosc.*, 1, 201