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Structural and spectroscopic characterization of methyl isocyanate, methyl cyanate, methyl fulminate, and acetonitrile N-oxide using highly correlated *ab initio* methods

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Various astrophysical relevant molecules obeying the empirical formula C_2H_3NO are characterized using explicitly correlated coupled cluster methods (CCSD(T)-F12). Rotational and rovibrational parameters are provided for four isomers: methyl isocyanate (CH_3NCO), methyl cyanate (CH_3OCN), methyl fulminate (CH_3ONC), and acetonitrile N-oxide (CH_3CNO). A CH_3CON transition state is inspected. A variational procedure is employed to explore the far infrared region because some species present non-rigidity. Second order perturbation theory is used for the determination of anharmonic frequencies, rovibrational constants, and to predict Fermi resonances. Three species, methyl cyanate, methyl fulminate, and CH_3CON , show a unique methyl torsion hindered by energy barriers. In methyl isocyanate, the methyl group barrier is so low that the internal top can be considered a free rotor. On the other hand, acetonitrile N-oxide presents a linear skeleton, C_{3v} symmetry, and free internal rotation. Its equilibrium geometry depends strongly on electron correlation. The remaining isomers present a bend skeleton. Divergences between theoretical rotational constants and previous parameters fitted from observed lines for methyl isocyanate are discussed on the basis of the relevant rovibrational interaction and the quasi-linearity of the molecular skeleton. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4963186>]

INTRODUCTION

Methyl isocyanate (MIC, CH_3NCO) is a well-known molecule because it was the principal toxicant involved in the Bhopal disaster, one of the largest toxic chemical catastrophe in world history. It is a relevant chemical compound for the production of carbamate pesticides, rubbers, and adhesives. As a result of its toxicity and volatility, it has been classified in the group of VOCs (Volatile Organic Compounds). In standard conditions, MIC is a liquid with melting and boiling point at $-45\text{ }^\circ\text{C}$ and $39.5\text{ }^\circ\text{C}$, respectively.¹

In addition to the atmospheric interest and applications, MIC is a relevant extraterrestrial molecule. In 2015, the Philae sounder of the *Rosetta* spacecraft landed on the 67P comet surface revealing the presence of various organic compounds. Methyl isocyanate was seen for the first time on a comet,² Very recently, after an extensive search, the molecule was also detected in gas phase sources^{3,4} although abundances are weakly correlated with those measured in the comet surface. Simultaneously, Halfen *et al.*³ discovered MIC in Sg B2(N) using the Arizona Radio Observatory Submillimeter Telescope, and Cernicharo *et al.*⁴ detected it in Orion.

Various MIC isomers are considered to be astrophysically detectable molecules.⁵ In general, excluding diatomic species, $\sim 30\%$ of all interstellar molecules have observed isomeric

counterparts.⁶ Accordingly, this paper attends to the MIC spectroscopic properties and to several organic compounds obeying the C_2H_3NO empirical formula such as methyl cyanate (MC, CH_3OCN), fulminate (FULM, CH_3ONC), acetonitrile N-oxide (AOX, CH_3CNO), and CH_3CON (MCON). Methyl isocyanate represents the most stable form. MC, FULM, and AOX are considered metastable species that can act as reaction intermediates. The stability of MCON is questionable.

The non-standard conditions of extraterrestrial sources could make possible the viability of low stability species. For C_2H_3NO isomers, the rotational line intensities and partition functions required for the assignments of the radioastronomical observations depend strongly on the low energy torsional and skeleton bending mode excitations.^{4,5} Three species, MC, FULM, and MCON, show a unique torsional mode hindered by energy barriers. In MIC, the methyl group barrier is so low that the methyl top can be considered a free rotor. On the other hand, AOX presents a linear skeleton, C_{3v} symmetry, and free internal rotation.

Unfortunately, few previous experimental and theoretical works attend to low stable isomers MC, FULM, and AOX.⁷⁻¹⁴ To our knowledge nothing has been said concerning MCON. Sakaizumi *et al.*⁷ first analyzed the methyl cyanate microwave spectrum and estimated the dipole moment to be $4.26(46)\text{ D}$ ($\mu_a = 4.07(6)$; $\mu_b = 1.24(40)$). Very recently, the millimeter wave spectrum (700 transitions within

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$J'' = 10\text{--}35$ and $K_a'' = 0\text{--}13$) was recorded deriving spectroscopic constants reproducing the spectrum close to the experimental uncertainty.⁵ Earlier, in 1995, Pasinszki and Wetwood⁸ synthesized MC and characterized it by HeI photoelectron spectroscopy, photoionization mass spectroscopy, and infrared spectroscopy for the first time. They used MP2/6-31G** and CIS/6-31G** to help assignments.

Pasinszki and Wetwood⁹ dedicated attention to the acetonitrile N-oxide molecule. They characterized it by ultraviolet photoelectron spectroscopy, photoionization mass spectroscopy, and mid-infrared spectroscopy and assigned observed bands to the fundamental transitions, as well as to several overtones and combination bands.⁹ Pasinszki *et al.*⁹ emphasized the strong dependence of AOX symmetry on the electron correlation observing that different levels of theory lead to a C_s equilibrium structure or turn out a C_{3v} geometry. The AOX microwave spectrum recorded in the ground state and in the two first excited bending states^{12,13} is consistent with a symmetric top.¹⁰⁻¹³ AOX was obtained as products of reactions of oxygen atoms and acetonitrile in solid argon.¹⁴

Methyl isocyanate is the isomer which has inspired more interest. First measurements of the microwave spectrum occur during the 1960s^{15,16} followed by the series of papers of Koput¹⁷⁻²⁰ and Kasten and Dreizler.²¹ Koput measured in the 8-40 GHz region using Stark spectroscopy. The analysis was accomplished in terms of the quasi-symmetric top molecule model, accounting explicitly for the large-amplitude CNC bending motion, and internal and overall rotation.^{17,18} Thus, he estimated the barrier to linearity to be 1049 cm^{-1} , the equilibrium CNC valence angle to be 140.2° ,¹⁷ and the V_3 barrier to be 20.62 cm^{-1} .¹⁸ The dipole moment dependence on the CNC bending was explored.

The analysis of the MIC rotational spectrum is especially arduous given the high density of low energy rovibrational states derived from excitations of the torsional and CNC bending modes.¹⁸ Cernicharo *et al.*⁴ recovered this analysis after noticing several previous uncertainties, sometimes larger than the experimental precision, relevant for the interpretation of the new astrophysical observations. New experiments⁴ were performed following different steps to identify line sequences and providing various sets of Watson's A-reduced Hamiltonian parameters (hyperfine resolved or unresolved). Rare coincidences between the sets and large differences with some previous assignments of Koput¹⁸ were obtained. Discrepancies in the determination of A rotational constant are not negligible ($A = 73\,849.2\text{ MHz}$ ¹⁸ and $128\,402.0(13)\text{ MHz}$ ⁴).

MIC structure was confirmed in a subsequent electron diffraction study by Anderson *et al.*²² Fateley and Miller observed far infrared transitions in gas phase.²³ The infrared and Raman spectra of the gas and solid phases were measured by Sullivan *et al.*²⁴ in the $3200\text{--}20\text{ cm}^{-1}$ and $3200\text{--}10\text{ cm}^{-1}$ regions, respectively. Reva *et al.*²⁵ recorded the infrared spectra of methyl isocyanate isolated in Ar, Xe, and N_2 matrices.

In this paper, we use explicitly correlated *ab initio* methods that usually provide very accurate rotational and torsional parameters²⁶⁻²⁹ for a theoretical characterization of the C_2H_3NO isomers at low temperatures. Equilibrium

structures, vibrational frequencies, and rovibrational parameters are determined. Special attention is given to the determination of torsional energy levels and rotational constants. These are compared with recent experimental data.

RESULTS AND DISCUSSION

Computational details

The electronic structure calculations, needs as inputs of the rovibrational calculations, were achieved using the codes Gaussian³⁰ and Molpro.³¹

Throughout the work, two different theoretical procedures were utilized. The torsional properties were computed with a variational procedure implemented in our own code ENEDIM.³²⁻³⁴ For this purpose, we used as inputs potential energy surfaces of reduced dimensionality. Explicitly correlated coupled cluster theory with singles and doubles substitutions augmented by a perturbative treatment of triple excitations (CCSD(T)-F12b),^{35,36} implemented in Molpro, was applied to characterize the equilibrium geometries and for computing potential energy surfaces. The rotational and rovibrational parameters, as well as energy states

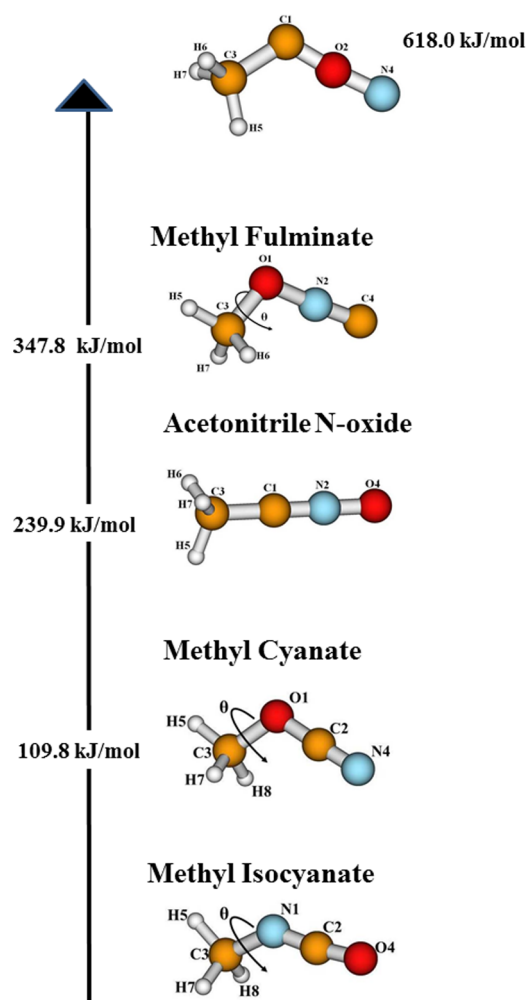


FIG. 1. Relative stabilities and atom labelling of methyl isocyanate and its isomers.

TABLE I. CCSD(T)-F12/AVTZ-F12 relative energies (E_r , in kJ/mol) and structural parameters (distances in Å and angles in degrees) of the C_2H_3NO isomers.

Methyl isocyanate CH_3-NCO Cs		Methyl cyanate CH_3-OCN Cs		Methyl fulminate CH_3-ONC Cs		(Transition state) CH_3-CON Cs	
E_r	0.0 ^a	E_r	110.5	E_r	351.5	E_r	631.0
ZPVE	130.5	ZPVE	129.0	ZPVE	126.7	ZPVE	120.0
$E_r + ZPVE$	0.0	$E_r + ZPVE$	109.8	$E_r + ZPVE$	347.8	$E_r + ZPVE$	818.0
C2N1	1.2038	C2O1	1.2926	O1N2	1.4449	C1O2	1.2489
C3N1	1.4454	C3O1	1.4511	C3O1	1.3246	C3C1	1.4926
O4C2	1.1744	N4C2	1.1632	C4N2	1.1773	N4O2	1.2345
H5C3	1.0864	H5C3	1.0842	H5C3	1.0855	H5C3	1.0871
H6C3 H7C3	1.0894	H6C3 H7C3	1.0881	H6C3 H7C3	1.0885	H6C3 H7C3	1.0926
C3N1C2	136.3	C3O1C2	113.4	C3O1N2	109.4	C3C1O2	124.4
O4C2N1	173.1	N4C2O1	178.7	O1N2C4	176.8	C1O2N4	163.8
H5C3N1	108.5	H5C3O1	105.3	H5C3O1	104.4	H5C3C1	108.7
H6C3N1 H7C3N1	110.7	H6C3O1 H7C3O1	109.5	H6C3O1 H7C3O1	109.6	H6C3C1 H6C3C1	110.9
H5C3N1C2	180.0	H5C3O1C2	180.0	H5C3O1N2	180.0	H5C3C1O2	180.0
H6C3N1H5- H7C3N1H5	119.3	H6C3O1H5- H7C3O1H5	119.2	H6C3O1H5- H7C3O1H5	119.3	H6C3C1H5- H7C3C1H5	119.3

^a $E = -207.734393$ a.u.

corresponding to the medium and high frequency vibrational modes, were explored using vibrational second order perturbation theory (VPT2)³⁷ implemented in Gaussian.³⁰ The VPT2 full-dimensional anharmonic force field was determined with second order Møller-Plesset theory (MP2).³⁸

The employed basis set was Dunning's type aug-cc-pVTZ³⁹ (denoted by AVTZ). For the explicitly correlated calculations, the MOLPRO default options were selected. The atomic orbitals were described by the AVTZ basis set in connection with the corresponding basis sets for the density fitting and the resolutions of the identity (the basis set

is denoted by AVTZ-F12). To obtain reliable equilibrium rotational constants, the core-valence electron correlation effects were introduced using CCSD(T) (coupled-cluster theory with singles and doubles substitutions, augmented by a perturbative treatment of triple excitations)⁴⁰ and the cc-pCVTZ basis set (denoted by CVTZ).⁴¹

Equilibrium geometries and rotational constants

A priori six structures type $CH_3-X-Y-Z$ ($X, Y, Z = C, N, O$) can be postulated. To confirm stabilities and for

TABLE II. Rotational constants (in MHz) and dipole moments (μ in D).

	B_e (CCSD(T)-F12)	ΔB_{vib} (MP2)	ΔB_{core} CCSD(T)	B_0	Expt.
Methyl isocyanate					
A	74 367.37	327.04	1469.90	76 164.32	73 849.2; ¹⁸ 78 395(410); ³ 128 402(13) ⁴
B	4401.56	10.61	-0.29	4411.89	4392.22; ¹⁸ 4442.982(49); ³ 4414.6287(75) ⁴
C	4267.29	-17.18	4.47	4254.58	4256.66; ¹⁸ 4256.691(31); ³ 4256.7452(71) ⁴
μ				3.2513	$\mu_a = 2.882(8)$ ²⁰
Methyl cyanate					
A	38 877.28	28.69	183.86	39 089.80	39 042.4(8); ⁷ 38 989.07 (20) ⁵
B	5336.45	-34.08	12.41	5314.78	5322.88(3); ⁷ 5322.25(15) ⁵
C	4837.49	-33.82	12.67	4816.35	4821.33(3); ⁷ 4821.31(13) ⁵ 4.26(46) ⁸
μ				4.9281	
Methyl fulminate					
A	37 120.42	161.03	161.03	37 004.74	
B	5704.58	15.61	15.61	5696.21	
C	5106.56	15.15	15.15	5083.48	
μ				3.8732	
CH_3-CON (transition state)					
A	64 907.63	175.26	375.4	65 458.29	
B	4550.54	-46.50	13.4	4517.44	
C	4369.91	-40.86	13.81	4342.86	
μ				2.6233	

TABLE III. Relative energies (E_r , in kJ/mol), structural parameters (distances in Å and angles in degrees), dipole moment (μ , in D), equilibrium rotational constants (in MHz), and CCSD(T)-F12 fundamental frequencies (ω , in cm^{-1}) of acetonitrile N-oxide (AOX, CH_3CNO).

	CCSD(T)/AVTZ-F12 C_{3v}				ω (Expt.)	
	Mode	Symm.	ω	Gas ⁸	Ar ¹⁴	
E_r^a	239.9	1	A_1	3055	2943	
C1C3	1.4623	2	A_1	2413	2311	2309
N2C1	1.1603	3	A_1	1429	1394	1381
O4N2	1.2151	4	A_1	1375	1348	1332
HxC3 (x = 5, 6, 7)	1.0891	5	A_1	788	785	780
H5C3C1 (x = 5, 6, 7)	110.2	6	E	3136	3022	
		7	E	1490	1453	
		8	E	1053	1034	
		9	E	489	477	
		10	E	108		
μ^b	5.4043				4.49 \pm 0.01 ⁷	
Rotational constants						
	B_e	ΔB_{core}		$B_e + \Delta B_{core}$	Expt. ¹²	
A	159 896.73	425.67		160 322.40		
B = C	3897.33	12.06		3909.39	3914.79 781(12)	

^a $E = -207.643\,056$ a.u.

^bCalculated with MP2/AVTZ.

a preliminary search of the minimum energy geometries, CCSD(T)-F12 calculations were achieved in connection with a smaller basis set than AVTZ-F12. Although this level of theory is considered to be too high for a preliminary scrutiny, we assumed that electron correlation could play an important role for many isomers. A species with formula $\text{CH}_3\text{-NOC}$ was not identified whereas $\text{CH}_3\text{-NCO}$ (MIC), $\text{CH}_3\text{-OCN}$ (MC), $\text{CH}_3\text{-CNO}$ (AOX), and $\text{CH}_3\text{-ONC}$ (FULM) were found to be stable species. All these ones present real harmonic frequencies, although their viability at standard conditions can be very low. Another species, $\text{CH}_3\text{-CON}$, behaves as an equilibrium structure when MP2 theory is employed and as a transition state (TS) when CCSD(T)-F12 is applied. We provide only its most relevant properties.

All the structures showing real harmonic frequencies are examined in this paper. The four isomers display very different structural and spectroscopic characteristics. At the CCSD(T)-F12 level of theory, MIC, MC, and FULM and the transition state MCON show bended skeletons, a single C_s conformer, and present non-rigidity. On the other hand, acetonitrile N-oxide, AOX, is a C_{3v} species with a linear skeleton, and it cannot be strictly considered a non-rigid molecule because the methyl group is a free rotor. In all the cases, the ground state potential energy surfaces show three equivalent minima. Figure 1 represents the four conformers and the transition state, their energy differences with respect to MIC and the atom labelling. The structural parameters of the non-rigid species and their rotational constants are shown in Tables I and II, respectively. Table III summarizes the corresponding properties of the linear AOX. Relative energies and geometries were determined with CCSD(T)-F12/AVTZ-F12 whereas the zero point vibrational energies (ZPVE) were calculated with MP2/AVTZ.

One fact with relevant effects on the rotational parameters is the linearity of the molecular skeleton. AOX shows a linear skeleton when its structure is determined with CCSD(T)-F12. However, it appears not be linear when MP2/AVTZ is used. These correlation effects were already emphasized.⁹ For the remaining structures, the angles between the heavy atoms are the following: $\text{C3N1C2} = 136.3^\circ$ and $\text{O4C2N1} = 173.1^\circ$ in MIC; $\text{C3O1C2} = 113.4^\circ$ and $\text{N4C2O1} = 178.7^\circ$ in MC; and $\text{C3O1N2} = 109.4^\circ$ and $\text{O1N2C4} = 176.8^\circ$ in FULM. At the equilibrium geometry, methyl isocyanate is the “least linear” molecule. These angles vary very slightly with the internal rotation.

TABLE IV. Rotational constants (in MHz) in the low excited vibrational levels.

Mode	ν (cm^{-1})	Assign.	A	B	C
Methyl isocyanate					
15	33	$\text{CH}_3\text{-t}$	72 944.22	4409.37	4266.24
10	171	CNC-b	83 247.16	4449.42	4254.79
14	589	NCO-b	65 247.98	4397.74	4256.41
Methyl cyanate					
15	149	$\text{CH}_3\text{-t}$	39 051.31	5299.88	4811.82
10	224	COC-b	39 867.67	5332.25	4820.97
14	502	CO-s	38 222.11	5305.96	4822.02
9	601	NCO-b	40 580.64	5320.50	4817.34
Methyl fulminate					
9	516	CON-b	37 001.42	5695.66	5031.54
10	190	CNOC-b	34 912.16	5686.43	5082.75
14	345	CNO-b	36 373.65	5679.35	5068.60
15	194	$\text{CH}_3\text{-t}$	38 431.55	5754.72	5047.37

TABLE V. CCSD(T)-F12b/AVTZ-F12 harmonic frequencies (ω , cm^{-1}), MP2/AVTZ anharmonic fundamentals (ν , cm^{-1}) and estimated band centers^a (ν , cm^{-1}) and IR intensities (I , $\text{D}^2/\text{\AA}^2 \text{ u}$).

Methyl isocyanate							
	Assign	ν	ω	Estimated band centers	I	Expt. ^{24,b}	
ν_1	A'	CH ₃ -s	3050	3152	3009	7.4	3030
ν_2		CH ₃ -s	2964	3053	2933	42.8	2968
ν_3		NC-s	2331	2334	2309	983.5	2230
ν_4		CH ₃ -b	1505	1515	1496	6.0	1483
ν_5		CH ₃ -b	1455	1479	1455	16.1	1434
ν_6		CH ₃ -b	1428	1459	1428	29.4	1402
ν_7		CH ₃ -b	1141	1163	1138	21.0	1130
ν_8		CN-s	862	889	868	24.9	855
ν_9		NCO-b	631	648	646	24.8	619
ν_{10}		CNC-b	170	177	171	19.5	172
ν_{11}	A''	CH ₃ -s	3032	3127	2990	10.9	3015
ν_{12}		CH ₃ -b	1515	1521	1505	7.1	1471
ν_{13}		CH ₃ -b	1123	139	1118	0.1	1114
ν_{14}		NCO-b	580	593	589	15.1	583
ν_{15}		CH ₃ -t	19	70	33	1.8	50
Methyl cyanate							
	Assign	ν	ω	Estimated band centers	I	Expt. ^{8,c}	
ν_1	A'	CH ₃ -s	3096	3194	3057	3.0	3042
ν_2		CH ₃ -s	3056	3065	3024	22.7	2968
ν_3		CN-s	2184	2305	2262	43.5	2263
ν_4		CH ₃ -b	1499	1509	1486	12.7	1470
ν_5		CH ₃ -b	1469	1478	1463	2.8	
ν_6		CH ₃ -b	1212	1237	1213	47.3	1213
ν_7		O-CN-s	1109	1138	1111	123.5	1112
ν_8		CO-s	884	911	885	27.3	893
ν_9		NCO-b	598	606	601	1.9	
ν_{10}		COC-b	220	225	224	7.3	
ν_{11}	A''	CH ₃ -s	3061	3156	3020	7.6	3017
ν_{12}		CH ₃ -b	1484	1503	1471	10.4	1462
ν_{13}		O-CN-s	1155	1179	1154	1.0	1152
ν_{14}		CO-s	492	506	502	6.4	
ν_{15}		CH ₃ -t	136	158	149	0.0	
Methyl fulminate							
	Assign	ν	ω	Estimated band centers	I		
ν_1	A'	CH ₃ -s	3092	3185	3048		
ν_2		CH ₃ -s	3048	3059	3016		
ν_3		NC-s	2041	2153	2110		
ν_4		CH ₃ -b	1504	1511	1492		
ν_5		CH ₃ -b	1456	1468	1451		
ν_6		HCO-b	1197	1225	1197		
ν_7		NO-s	1042	1063	1036		
ν_8		CO-s	880	884	866		
ν_9		CON-b	516	514	507		
ν_{10}		CNOC-b	190	171	175		
ν_{11}	A''	CH ₃ -s	3057	3150	3014		
ν_{12}		CH ₃ -b	1459	1490	1445		
ν_{13}		CH ₃ -b	1151	1175	1149		
ν_{14}		CNO-b	345	321	321		
ν_{15}		CH ₃ -t	194	197	191		

^aFermi displacements $\Delta\nu > 10 \text{ cm}^{-1}$ (emphasized in bold).^bGas phase IR and Raman spectra.^cGas phase IR spectrum.

TABLE VI. MP2/AVTZ centrifugal distortion constants.^a

	Methyl isocyanate		Methyl cyanate		Methyl fulminate Calc.
	Calc.	Expt. ³	Calc.	Expt. ⁴	
Δ_J (kHz)	0.76	2.323 19(98)	3.4815	3.409 65(66)	2.976
Δ_K (kHz)	55 230.93		1854.50	1727(23)	396.96
Δ_{JK} (kHz)	1336.15	-1271.46(73)	-104.61	-81.406(10)	139.95
δ_J (kHz)	-0.262	0.4038(14)	0.819	0.791 49(89)	0.422
δ_K (kHz)	226.14	187.4(35)	-1.01	1.72(11)	73.82
Φ_J (Hz)	0.000 669	-0.001 42(45)	0.012	0.010 09(28)	0.004
Φ_K (Hz)	-126 755.58		0.312		54.14
Φ_{JK} (Hz)	11.59	-5.64(18)	-0.103	-0.2671(36)	4.06
Φ_{KJ} (Hz)	4865.04	-67 991.(167)	-17.05	-8.249(66)	-12.83
ϕ_I (Hz)	-0.000 689		0.005	0.004 57(39)	-0.003
ϕ_K (Hz)	-5938.10		31.13		71.12
ϕ_{JK} (Hz)	11.340	-47.7(14)	0.30		1.96

^aA-reduction Hamiltonian (Γ) parameters.

The CCSD(T)-F12/AVTZ-F12 equilibrium rotational constants of Table II were employed to determine the corresponding ground state parameters with the straightforward formula^{26–29}

$$B_0 = B_e + \Delta B_e^{\text{core}} + \Delta B^{\text{vib}}, \quad (1)$$

where ΔB^{vib} represents the vibrational contribution to the rotational constants derived from the VPT2 α_r^i vibration-rotation interaction parameters determined using the MP2 cubic force field (see below), and ΔB_e^{core} is computed from $B_e(\text{CV})$ and $B_e(\text{V})$ which were calculated correlating both core and valence electrons (CV) or just the valence electrons (V) in the post-SCF process,

$$\Delta B_e^{\text{core}} = B_e(\text{CV}) - B_e(\text{V}). \quad (2)$$

For MIC and MC, the computed parameters A_0 , B_0 , and C_0 are compared with experimental data from Refs. 3–5 and 18. In general, the agreement is very good with the exception of the MIC A_0 rotational constant. This parameter has been calculated to be 76 164.32 MHz far away from the fitted value of Cernicharo *et al.*⁴ (128 402 (13) MHz), using the AABS package for Assignment and Analysis of Broadband Spectra.^{42,43} The difference $|A_0^{\text{ab initio}} - A_0^{\text{exp}}|$ reaches 52 237 MHz.⁴ A better agreement is obtained with the parameters fitted by Koput¹⁸ and Halfen *et al.*,³ although the differences $|A_0^{\text{ab initio}} - A_0^{\text{exp}}| = 2315$ MHz¹⁸ and $|A_0^{\text{ab initio}} - A_0^{\text{exp}}| = 2231$ MHz³ are too large if we compare them with the usual accuracy found when CCSD(T)-F12 theory is applied.^{26–29} This method usually provides a precision of few MHz.

The divergence obtained for A_0 contrasts with what is obtained for B_0 and C_0 . For these two parameters, $|B_0^{\text{ab initio}} - B_0^{\text{exp}}| = 20$ MHz,¹⁸ 31 MHz,³ 3 MHz,⁴ and $|C_0^{\text{ab initio}} - C_0^{\text{exp}}| = 2$ MHz^{3,4,18} which represents an expected accuracy.

In Table I, the MP2/AVTZ dipole moments ($\mu = 3.2513$ D (MIC); $\mu = 4.9281$ D (MC)) are shown. Experimental values are available for MIC ($\mu = 2.88$ D),¹⁶ for MC ($\mu = 4.26(46)^7$),

and for AOX ($\mu = 4.49$ D⁹). Differences between MP2 and experimental values are of a reasonable order of magnitude given the expected accuracy of the employed techniques.

Finally, Tables I and II collect structural parameters and rotational constants of the $\text{CH}_3\text{-CON}$ species which is described as an isomers when MP2 theory is used and as a transition state when CCSD(T)-F12 calculations are applied. Both levels of theory lead to different equilibrium geometries. The angle H5C3C1O2 describing the methyl torsion is found to be 0.0° or 180° depending on the level of theory.

Full-dimensional anharmonic analysis

Tables IV–VI summarize relevant VPT2 spectroscopic parameters. The harmonic contributions were determined at the CCSD(T)-F12 level of theory whereas a MP2/AVTZ anharmonic force field was used to compute the anharmonic corrections.

Table IV displays the rotational constants determined in the first excited vibrational levels corresponding to the torsional and the skeletal bending modes. They were computed using the CCSD(T)-F12 equilibrium parameters and Eq. (1). The vibrational contributions ΔB^{vib} were determined at the MP2 level of theory. The large dependence of the methyl isocyanate A rotational constant on the vibrational energy ($A_0 = 76 164.32$ MHz and $A(v_{10} = 1) = 83 247.16$ MHz) must be highlighted. It can be the origin of the large discrepancies observed in the fitted parameters of the effective Hamiltonians employed for the assignments of MIC spectra.^{3,4,18} Perhaps, neglected high order terms describing the rotational-vibrational interaction are mandatory. Assignments of methyl cyanate fulminate which behaviors are customary, are easy.

Table V summarizes the CCSD(T)-F12/AVTZ-F12 harmonic and the MP2/AVTZ anharmonic fundamentals of all the isomers and all the vibrational modes. The band center

positions were estimated combining both levels of theory. For MIC and MC, computed values are compared with the band center positions of the gas phase IR and Raman spectra measured by Sullivan *et al.*²⁴ and the gas phase IR spectrum of Pasinszki and Westwood.⁸ With few exceptions, there is an agreement between computed and observed band centers. It has to be taken into consideration that VPT2 is not a proper theory to characterize torsional states. Fermi interactions are predicted using the algorithms implemented in Gaussian.³⁰ Band suffering relevant displacements are emphasized in bold.

Finally, Table VI collects set of centrifugal distortion constants. They are parameters of the Γ representation of the A-Watson reduction Hamiltonian. For MIC and MC, computed data are compared with the experimental ones from Refs. 4 and 5. The cubic terms of the anharmonic force field were used to predict possible Fermi displacements using the Gaussian 09 algorithms.³⁰ Significant interactions

between levels of the out-of-plane torsional modes and the remaining vibrational energies including the large amplitude bending modes are not expected. This supports the use of one-dimensional operators for torsional energy computations.

Torsional energy levels

The torsional energy levels of MIC, MC, and FULM were computed by solving variationally the following one-dimensional Hamiltonian:

$$\hat{H}(\theta) = -\left(\frac{\partial}{\partial\theta}\right)B_{\theta}(\theta)\left(\frac{\partial}{\partial\theta}\right) + V^{\text{eff}}(\theta). \quad (3)$$

The validity of the one-dimensional model is supported by the test of the Fermi interactions performed with the algorithms implemented in Gaussian. The θ independent coordinate was defined with the following linear combination:

$$\begin{aligned} \theta(\text{MIC}) &= (\text{H5C3N1C2} + \text{H6C3N1C2} + \text{H7C3N1C2})/3 - 180^{\circ}, \\ \theta(\text{MC}) &= (\text{H5C3O1C2} + \text{H6C3O1C2} + \text{H7C3O1C2})/3 - 180^{\circ}, \\ \theta(\text{FULM}) &= (\text{H5C3O1N2} + \text{H6C3O1N2} + \text{H7C3O1N2})/3 - 180^{\circ}. \end{aligned} \quad (4)$$

In Eq. (2), $B_{\theta}(\theta)$ are the kinetic energy parameter, and V^{eff} the effective potential energy surface,

$$V^{\text{eff}}(\theta) = +V(\theta) + V'(\theta) + V^{\text{ZPVE}}(\theta). \quad (5)$$

$B_{\theta}(\theta)$ are the G matrix elements in cm^{-1} .³³ They were determined using the *ab initio* geometries and the algorithms implemented in the ENEDIM code.³² The values corresponding to the selected coordinates were fitted to Fourier expansions formally identical to the potential energy surfaces. Details concerning the procedure can be found in Ref. 33. Then,

$$B_{\theta}(\text{MIC})^{\text{eff}}(\theta) = 8.5991 - 0.0002 \cos 3\theta - 0.0057 \cos 6\theta,$$

$$B_{\theta}(\text{MC})^{\text{eff}}(\theta) = 6.1332 - 0.0264 \cos 3\theta + 0.0008 \cos 6\theta,$$

$$B_{\theta}(\text{FULM})^{\text{eff}}(\theta) = 6.0545 - 0.0423 \cos 3\theta.$$

$V(\theta)$ is the *ab initio* one-dimensional potential energy surface; $V'(\theta)$ and $V^{\text{ZPVE}}(\theta)$ represent the pseudopotential and the zero point vibrational energy correction,⁴⁴ respectively. Kinetic and potential energy parameters were computed and fitted to Fourier series using the ENEDIM code³²⁻³⁴ and the energies, geometries, and harmonic frequencies of a set of partially optimized structures. The analytical expressions of the V^{eff} potentials (in cm^{-1}) are the following:

$$V(\text{MIC})^{\text{eff}}(\theta) = 13.458 - 8.113 \cos 3\theta + 1.656 \cos 6\theta,$$

$$V(\text{MC})^{\text{eff}}(\theta) = 191.912 - 189.412 \cos 3\theta - 2.5 \cos 6\theta,$$

$$V(\text{FULM})^{\text{eff}}(\theta) = 416.792 - 410.871 \cos 3\theta - 5.921 \cos 6\theta.$$

(6)

The effective potentials are represented in Figures 2 and 3; the barrier heights and the independent coefficients of the kinetic energy parameters and the calculated torsional energy levels are shown in Table VII. Methyl torsional energy barriers are radically different ($V_3(\text{MIC}) = 16.2 \text{ cm}^{-1}$; $V_3(\text{MC}) = 364.8 \text{ cm}^{-1}$; $V_3(\text{FULM}) = 821.7 \text{ cm}^{-1}$). For comparison, we provide some previous values determined for other systems containing methyl groups: the MCON transition state ($V_3 = 22.8 \text{ cm}^{-1}$ [this work]), acetaldehyde ($V_3 = 412.7 \text{ cm}^{-144}$), methylamine ($V_3 = 708.6 \text{ cm}^{-145}$), methanol ($V_3 = 377.9 \text{ cm}^{-146}$), dimethyl-ether ($V_3 = 950.6 \text{ cm}^{-147}$), and acetone ($V_3 = 267 \text{ cm}^{-148}$).

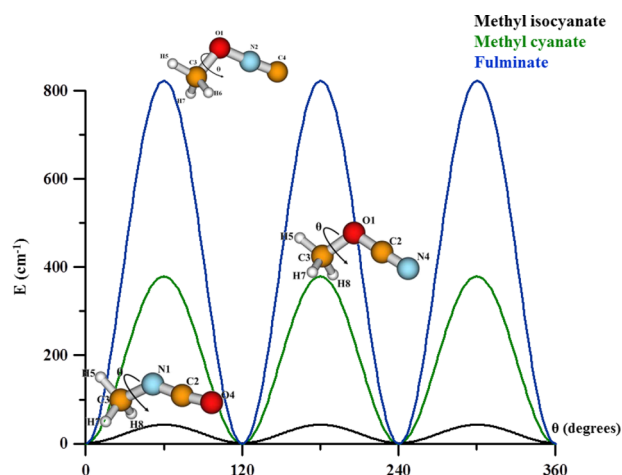


FIG. 2. Comparison between the 1D-potential energy functions of methyl isocyanate, methyl cyanate, and methyl fulminate.

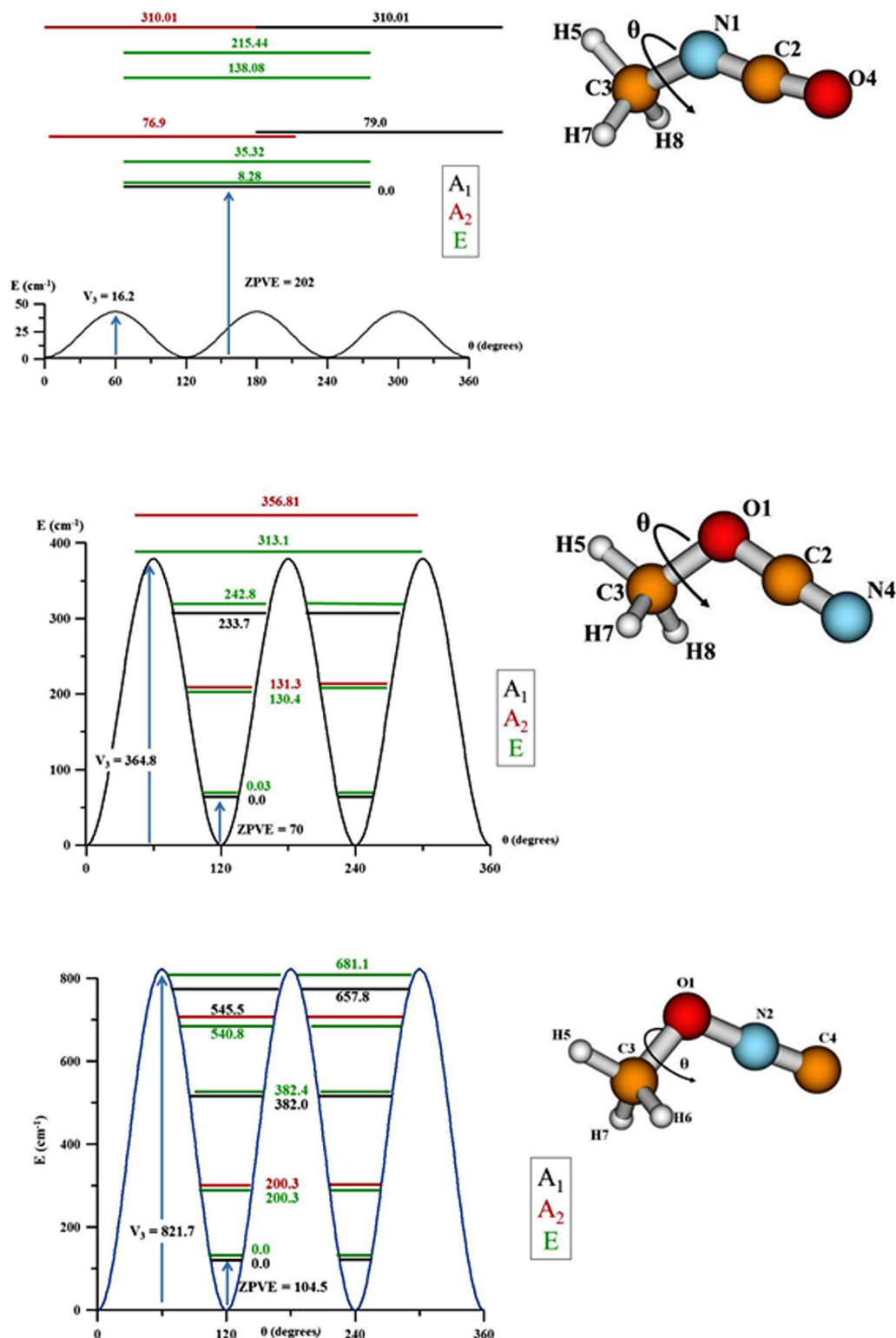


FIG. 3. One dimension potential energy surface and torsional energy levels (in cm^{-1}) of methyl isocyanate, methyl cyanate, and fulminate.

Torsional energy levels are represented in Figure 3. All the calculated energies of MIC are found above the torsional barrier. This causes a particular distribution of the energies coincident with previous estimations of Koput.¹⁸ The fundamental torsional frequency $0 \rightarrow 1$ was determined to be 76.9 cm^{-1} ($A_1 \rightarrow A_2$) and 27.04 cm^{-1} ($E \rightarrow E$). The splitting

of $\nu = 0$ was evaluated to be 8.28 cm^{-1} . On the other hand, the methyl cyanate fundamental was predicted at 131.27 cm^{-1} ($A_1 \rightarrow A_2$) and 130.34 cm^{-1} ($E \rightarrow E$), and the splitting of $\nu = 0$ to be 0.03 cm^{-1} . The corresponding energies of methyl fulminate are obtained to be 200.33 cm^{-1} ($A_1 \rightarrow A_2$) and 200.21 cm^{-1} ($E \rightarrow E$).

TABLE VII. Torsional energy levels and parameters (in cm^{-1}) calculated with CCSD(T)-F12. Potential and kinetic parameters.

v	MIC CH ₃ -t			MC CH ₃ -t	FULM CH ₃ -t
	Symm.	E	Expt. ¹⁸	E	E
0	A ₁	0.0	0.0	0.0	0.0
	E	8.28	8.4	0.03	0.0
1	A ₂	76.9	79.7	131.27	200.33
	E	35.32	36.8	130.37	200.31
2	A ₁	79.0	80.3	233.72	382.04
	E	138.08	140.6	242.75	382.43
3	A ₂	310.01	311.1	356.81	545.54
	E	215.44	217.5	313.10	540.75
4	A ₁	310.02	311.1	373.65	657.75
	E	421.80		438.59	681.13
5	A ₂	696.96		627.82	843.19
	E	550.78		526.33	765.71
6	A ₁	696.96		627.96	855.49
	E	860.34		742.56	954.16
7	A ₂	1238.69		1010.07	1208.30
	E	1040.92		870.01	1074.21
8	A ₁	1238.69		1010.07	1208.41
	E	1453.67		1162.61	1385.55
ZPVE		202.0		69.98	104.5
B ₀ ^a		8.5991		6.1332	6.0545
V ₃		16.23	20.62	364.84	821.74

^aB₀ represents the coordinate independent term of the B₀(θ) expansion.

CONCLUSIONS

Spectroscopic and structural properties are determined for methyl isocyanate, methyl cyanate, methyl fulminate, and acetonitrile N-oxide using explicitly correlated coupled cluster methods. We provide relative energies, as well as rotational, rovibrational, and torsional parameters considering that rotational line intensities and partition functions required for the assignments of the radioastronomical observations depend strongly on the low energy torsional and skeleton bending mode excitations. There are four essentials that can be emphasized:

1. *A priori* six structures type CH₃-X-Y-Z (X, Y, Z = C, N, O) can be postulated, but only four CH₃-NCO (MIC), CH₃-OCN (MC), CH₃-CNO (AOX), and CH₃-ONC (FULM) represent stable species. CH₃-NOC was not identified, and CH₃-CON behaves as an equilibrium structure when MP2 theory is employed and as a transition state when CCSD(T)-F12 is applied.
2. The CCSD(T)-F12 equilibrium rotational constants of acetonitrile N-oxide, A_e = 160 322.4 MHz, B_e = C_e = 3909.39 MHz, correspond to a C_{3v} structure. The remaining isomers present a bended skeleton and non-rigidity caused by internal rotation. The most stable isomer, methyl isocyanate, contains a rotating methyl group that can be considered a free rotor given the very low torsional energy barrier (V₃ = 16.2 cm^{-1}). Torsional and rotational parameters are computed for methyl cyanate (V₃ = 364.84 cm^{-1} , A₀ = 39 089.80 MHz, B₀ = 5314.78 MHz, and C₀ = 4816.35 MHz) and methyl

fulminate (V₃ = 821.7 cm^{-1} , A₀ = 37 004.74 MHz, B₀ = 5696.21 MHz, and C₀ = 5083.48 MHz).

3. With the exception of the MIC A₀ rotational constant, an excellent agreement is found with previous experimental parameters. The difference $|A_0^{ab\text{ initio}} - A_0^{\text{exp}}| > 2000$ MHz is unacceptable given the usual accuracy of the CCSD(T)-F12 method. The large dependence of the methyl isocyanate A rotational constant on the vibrational energy can be the origin of the large discrepancies. The quasi-linearity of MIC cannot explain this divergence because MIC is the “least linear isomer”. The skeleton structure varies slightly with the internal rotation.

In this work, we provide sets of spectroscopic parameters obtained using highly correlated *ab initio* methods. We believe that our parameters can be used as starting points for the fitting of the effective Hamiltonians employed for spectra assignments. Both rotational and torsional parameters are provided because at very low temperatures, the low energy levels can be populated. The calculated parameters allow to compare the different isomers. Whereas MC and FULM show predictable behaviors, MIC represents a “tricky species” where some data, i.e., the A rotational constant, present an unexpected behavior. Future MIC studies require strong collaborations between theory and experiments to define properly the terms of the effective Hamiltonians.

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