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Effect of Ionization on Infrared and Electronic Absorption Spectra of Methyl and Ethyl Formate in the Gas Phase and in Astrophysical H₂O Ice: A Computational Study

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ABSTRACT: This work reports infrared and electronic absorption spectra of trans and gauche conformers of neutral ethyl formate, trans and cis conformers of neutral methyl formate, their ions in the gas phase, and neutral ethyl and methyl formate in astrophysical H₂O ice. The second-order Møller–Plesset perturbation (MP2) method with TZVP basis set has been used to obtain ground-state geometries. An influence of ice on vibrational frequencies of neutral ethyl and methyl formate was obtained using integral equation formalism polarizable continnum model (IEFPCM). Significant shift in vibrational frequencies for neutral methyl and ethyl formate when studied in H₂O ice and upon ionization is observed. Rotational and distortion constants for neutral ethyl and methyl formate from this work are in excellent agreement with the available experimental values. Electronic absorption spectra of conformers of ethyl and methyl formate and their ions are obtained using time-dependent density functional method (TDDFT). The nature of electronic transitions is also identified. We suggested lines especially good to detect these molecules in interstellar medium. Using these lines, we can identify the conformers of ethyl and methyl formate in gas phase and H₂O ice in interstellar medium. This comparative study should provide useful guidelines to detect conformers of ethyl and methyl formate and their ions in gas phase and neutral molecules in H₂O ice in different astronomical environment.
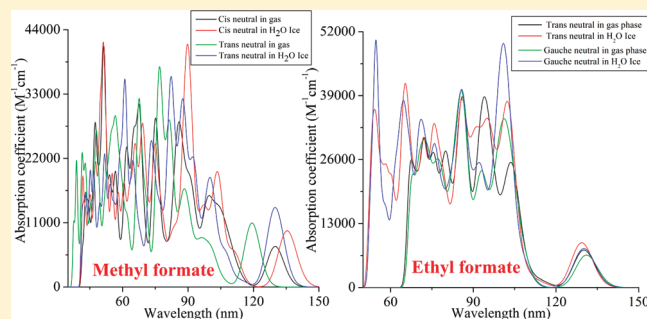
1. INTRODUCTION

Interstellar medium and intergalactic medium contain a certain level of matter in the form of gas and tiny solid particles over a wide range of physical conditions.[1] The dust takes the form of silicate and carbonaceous solids, and gas consists of atoms and molecules.[2,3] About half of the interstellar medium in our galaxy is in molecular form and its remaining half in neutral hydrogen clouds. Molecules are formed in a variety of environments such as circumstellar shells,[4,5] diffuse interstellar medium[6] and giant molecular clouds. Through their electronic, vibrational, and rotational spectra, it is possible to identify interstellar molecules in space.[7−9] More than 150 molecules have been detected in space so far.[10−12] To learn about the composition of the dust and gas as well as to extract physical parameters, spectroscopic characterizations of molecules are necessary. The scientific literature concerned with the spectroscopic characterization of interstellar molecules is growing rapidly. It includes small molecules[13−15] as well as large molecules such as polycyclic aromatic hydrocarbons (PAHs).[16−19] Despite this rapid progress, many new and potentially important molecules are still to be detected in space particularly the astrobiologically relevant molecules such as amino acids.[20] It is possible to detect many more molecules in space if we have their complete spectroscopic characterization. Theoretical methods such as quantum chemical methods help in this task.

Ethyl formate (C₂H₅OCHO), also known as formic acid ethyl ester or ethyl methanoate, is one of the possible interstellar molecules since methyl formate has already been detected in space.[16,21−24] Ethyl formate can be synthesized in the hot core phase starting from the well-known hot core molecule ethanol. The protonation reaction takes place for formation of ethyl formate.[25] Microwave spectrum of ethyl formate has shown that there are two possible conformers of ethyl formate, namely, trans and gauche conformers.[26] Karpovitch and Tabuchi have studied this molecule in liquid phase using ultrasound dispersion measurements.[27,28] Peng et al.[29] have studied the structure of ethyl formate using gas-phase electron diffraction, microwave, and infrared data.[29] The rotational spectrum of ethyl formate has been reported for both microwave[27,30,31] and millimeter wave range.[32,33] Out of several possible conformers of ethyl formate, only trans and gauche conformers have been detected experimentally.[27,29,34,35] Ethyl formate has also been detected in space recently in extremely active region of high-mass star formation Sagittarius B2 (N).[36] Depending upon the physical circumstances, this molecules may be in neutral (trans and gauche) or ionic form in space.

Methyl formate is a typical hot core molecule. It is very abundant in massive star forming region and was detected first in the Sgr B2 region using microwave transitions.[37] The

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microwave spectrum of methyl formate in the frequency range of 8—58 GHz was reported by Bauder.[38] Plummer et al.[39] have used the theory of solely semirigid asymmetric top Hamiltonian to fit the rotational lines of methyl formate in the ground state at high J transitions belonging to the symmetric sublevel with the accuracy ≤ 0.1 MHz. Over 250 rotational transitions of the internal rotor methyl formate in its ground state, degenerate torsional substates have been measured in the millimeter wave spectral region.[40] The ideal gas thermodynamic properties of 44 key organic oxygen compounds in the carbon range C_1 to C_4 have been calculated[41] using statistical mechanical technique and methyl formate is one of those 44 organic compounds. The forbidden lines of methyl formate are reported along the c-principal axis which does not possess dipole moment except for the perturbative influence of internal rotation (torsional motion) by Plummer et al.[42] The microwave spectrum of methyl formate has been observed by Odashima et al.[43] in the frequency range of 7—200 GHz, and new 437 lines have been assigned to the first excited A torsional substate. A total of 3514 lines were fitted by them to the 10th-order reduced Hamiltonian model involving 67 molecular parameters to a 1σ standard deviation of 179 kHz. Methyl formate was also detected in the low-mass star forming region.[24]

Torsionally excited methyl formate in Orion KL was studied by Kobayashi et al.[44] A large number of newly measured rotational torsional transitions in the ground A and E torsional substates have been combined with the previous data set of 2482 lines consisting of transitions involving $j \leq 50$ by Oesterling et al.[45] According to Senent et al.[46] there are two conformers (cis and trans) of methyl formate which differ in energy by 5.3 kcal mol^{-1}.[46] Carvajal et al.[47] have reinvestigated the laboratory spectrum for the methyl formate molecule involving both the ground and first excited torsional states. Recently the microwave spectrum of monodeuterated methyl formate HCOOCH$_2$D was measured in three regions by Fourier transform microwave spectroscopy and global fit within experimental accuracy of microwave rotational transitions in the ground and first excited torsional states (V_t = 0 and 1) of methyl formate was reported.[48,49]

Ethyl and methyl formate molecules detected in interstellar medium so far are in neutral form. Depending upon the astronomical environment, molecules may be in neutral or ionized form. These molecules may be present in gas phase or in H_2O ice medium. The spectroscopic characterization of all forms, viz., neutral, cationic, and anionic forms of trans and gauche conformers of ethyl formate and trans and cis conformers of methyl formate in gas phase and H_2O ice is essential in order to detect these molecules in space. To detect their ions and those in H_2O ice, knowledge of a change in spectra of neutral molecules upon ionization and in H_2O ice will be helpful. To our knowledge, thorough spectroscopic characterizations of ethyl and methyl formate and their ions in gas and H_2O ice have not been done so far.

The aim of this work is to study ethyl formate (gauche and trans), methyl formate (trans and cis) in neutral and ionic forms in gas phase, and neutral molecules in H_2O ice using quantum chemical method. We predict theoretical, vibrational, and electronic absorption spectra of neutral ethyl and methyl formate molecules, their ions, and neutral molecules in astrophysical H_2O ice. This study will help in the interpretation and analysis of the observational data obtained for different environment. This paper is organized as follows. The next section gives computational details. Vibrational and electronic absorption spectra of
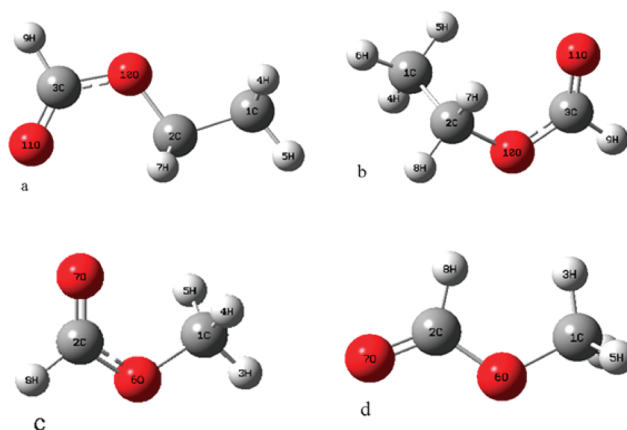

Figure 1. (a) Trans and (b) gauche conformers of ethyl formate and (c) trans and (d) cis conformers of methyl formate optimized at the MP2/TZVP level of theory.

ethyl and methyl formate along with astrophysical implications are discussed in Results and Discussion. Conclusions are inferred in the last section.

2. COMPUTATIONAL DETAILS

Geometries of trans and gauche conformers of neutral ethyl formate, trans and cis conformers of neutral methyl formate, and their ions are optimized at second-order Møller—Plesset (MP2) perturbation theory using the TZVP basis set.[50−54] The trans and gauche conformers of neutral ethyl formate and their ions are obtained on the basis of $C_1C_2O_{10}C_3$ dihedral angle[29] as shown in Figure 1. The trans and cis conformers of methyl formate are obtained on the basis of $C_1O_6C_2O_7$ dihedral angle[47] as shown in Figure 1. To study ethyl and methyl formate molecules in H_2O ice, we optimized geometries of neutral ethyl and methyl formate at MP2/TZVP level of theory using integral equation formalism polarizable continuum model (IEFPCM)[55−57] with dielectric constant 78.5.[58] Since the dielectric constant of ice (85.5) is slightly higher than that of water (78.5), the vibrational frequencies reported here are not exactly for ice but close to those in ice. The scaling factors for vibrational frequencies are not very sensitive to the basis set, so for this level of theory we have used a scaling factor of 0.953.[59] Time-dependent density functional theory (TDDFT) calculations were performed for excited states of neutral and charged ethyl and methyl formate at the same level of theory. The nature of electronic transitions was identified. The SWizard program was used to obtain the percent contribution from each transition.[60] All of the calculations were performed using Gaussian 03 program package.[61]

3. RESULTS AND DISCUSSION

The conformers of ethyl formate (trans and gauche) and methyl formate (trans and cis) are optimized at the MP2/TZVP level and are shown in Figure 1. Bond lengths, angles, and dihedral angles for the neutral and ionized trans and gauche conformers of ethyl formate in gas phase and neutral ethyl formate in H_2O ice are presented Table 1. In Table 2, bond lengths, angles, and dihedral angles for neutral and charged trans and cis conformers of methyl formate and neutral methyl formate in H_2O ice are represented. The ionization potential as well as electron affinity for the two conformers of ethyl formate are

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Table 1. Optimized Geometries for Neutral, Cation, and Anion of Trans and Gauche Conformers of Ethyl Formate at MP2/TZVP Level of Theory in Gas Phase and H$_2$O Ice (Bond Lengths, Å; Angles, deg)

	trans				gauche			
parameter	neutral H$_2$O ice	neutral gas phase	cation	anion	neutral H$_2$O ice	neutral gas phase	cation	anion
C$_3$=O$_{11}$	1.207	1.207	1.275	1.263	1.207	1.207	1.275	1.271
C$_3$−O$_{10}$	1.341	1.341	1.252	1.509	1.341	1.341	1.251	1.518
C$_2$−O$_{10}$	1.446	1.446	1.530	1.396	1.448	1.448	1.528	1.400
C$_2$−C$_1$	1.508	1.508	1.495	1.519	1.513	1.513	1.501	1.527
C$_3$−H$_9$	1.094	1.091	1.094	1.114	1.094	1.094	1.095	1.113
C$_2$−H	1.089	1.089	1.088	1.103	1.087	1.088	1.081	1.096
C$_1$−H	1.089	1.088	1.087	1.091	1.088	1.087	1.088	1.095
∠O$_{10}$-C$_3$=O$_{11}$	125.8	125.8	125.1	117.3	126.2	126.2	125.6	117.1
∠C$_2$-O$_{10}$-C$_3$	114.8	114.8	119.4	110.8	115.5	115.5	120.3	111.2
∠C$_1$−C$_2$-O$_{10}$	107.2	107.2	106.4	108.7	111.4	111.4	110.2	113.1
∠H$_9$−C$_3$=O$_{11}$	124.9	124.9	114.8	121	124.8	124.8	114.6	121.0
∠O$_{10}$−C$_2$−H(CH$_2$)	108.7	107.7	105.5	110.6	106.3	108.8	105.3	106.8
∠C$_2$−C$_1$−H(CH$_3$)	110.2	109.4	111.0	110.5	110.1	109.4	106.8	109.2
φ(C$_2$−O$_{10}$−C$_3$−O$_{11}$)	0	0	0.06	−46.4	0.97	0.9	0.4	37
φ(C$_1$−C$_2$−O$_{10}$−C$_3$)	179.9	179.9	−165.6	178.2	81.2	81.2	70.6	71.6

Table 2. Optimized Geometries for Neutral, Cation, and Anion of Trans and Cis Conformers of Methyl Formate at the MP2/TZVP Level of Theory in Gas Phase and H$_2$O Ice (Bond Lengths, Å; Angles, deg)

	trans				cis			
parameter	neutral H$_2$O ice	neutral gas phase	cation	anion	neutral H$_2$O ice	neutral gas phase	cation	anion
C$_1$−H(CH$_3$)	1.089	1.090	1.083	1.099	1.083	1.086	1.083	1.096
C$_1$−O$_6$	1.433	1.433	1.494	1.390	1.498	1.436	1.498	1.397
C$_2$−O$_6$	1.346	1.346	1.251	1.504	1.254	1.341	1.254	1.501
C$_2$−H$_8$	1.105	1.105	1.096	1.130	1.094	1.093	1.096	1.114
C$_2$−O$_7$	1.193	1.193	1.274	1.260	1.273	1.207	1.273	1.271
∠O$_6$−C$_1$−H(CH$_3$)	109.4	109.4	106.2	111.1	106.1	108.6	106.1	110.5
∠C$_2$−O$_6$−C$_1$	118.3	118.3	119.9	109.7	119.5	114.3	119.5	110.2
∠H$_8$−C$_2$−O$_6$	113.1	113.1	125.3	103.9	119.7	109.1	124.9	117.4
∠O$_7$−C$_2$−O$_6$	122.8	122.8	120.7	115.1	124.9	125.7	119.7	101.1
φ(C$_1$O$_6$C$_2$O$_7$)	179.9	179.9	179.9	174.1	0.016	−0.001	0.016	−45.2

found to be equal, viz., 246.2 and 42.2 kcal mol^{-1}, respectively. The trans conformer of ethyl formate is lower in energy by 0.091 kcal mol^{-1} than the gauche conformer. The ionization potential as well as electron affinity for the two conformers of methyl formate are found to be equal, viz., 246.7 and 40.3 kcal mol^{-1}, respectively. The cis conformer of methyl formate is lower in energy by 5.8 kcal mol^{-1} than the trans conformer which is in agreement with the experimental value of 4.8 kcal mol^{-1}.[62] The dipole moments of trans and gauche conformer of neutral ethyl formate from this work are 2.21 and 2.0 D, respectively, and comparable with respective experimental value of 1.98 ± 0.02 and 1.81 ± 0.02 D.[29]

3.1. Structural Changes in Ethyl and Methyl Formate. As can be seen from Table 1, geometrical parameters change significantly upon ionization of trans and gauche conformer of ethyl formate. The dihedral angle C$_1$C$_2$O$_{10}$C$_3$ has changed from +180 to −165° in cation of trans conformer and in anion the dihedral angle C$_2$O$_{10}$C$_3$O$_{11}$ has changed from 0 to −46.4°. In anion of gauche conformer the dihedral angles C$_2$O$_{10}$C$_3$O$_{11}$ and C$_1$C$_2$O$_{10}$C$_3$ have changed from 0.9 to 37.0° and from 81.2 to

71.6°, respectively. Not only dihedral angles but bond lengths and angles have also changed significantly upon ionization for both, trans and gauche conformers of ethyl formate. Bond lengths C$_3$O$_{11}$, C$_3$O$_{10}$, and C$_2$O$_{10}$ and angles O$_{10}$C$_3$O$_{11}$, C$_2$O$_{10}$C$_3$, and H$_9$C$_3$O$_{11}$ have changed upon ionization in both the conformers. There is no significant change observed in bond lengths, angles, and dihedral angles in both the conformers of ethyl formate in gas phase and H$_2$O ice.

The geometrical parameters of trans and cis conformers of methyl formate and their ions in gas phase and H$_2$O ice are reported in Table 2. Geometrical parameters for neutral trans and cis conformers of methyl formate in gas phase and in H$_2$O ice are almost equal whereas those change significantly in the anion of cis conformer. In anion of cis conformer the dihedral angle C$_1$O$_6$C$_2$O$_7$ has changed from +0.016 to −45.2°. A change in C$_1$−O$_6$, C$_2$=O$_6$, C$_2$−H$_8$, and C$_2$=O$_7$ bond lengths and O$_6$−C$_1$−H, C$_2$−O$_6$−C$_1$, and H$_8$−C$_2$−O$_6$ bond angles is also observed upon ionization in both of the conformers of methyl formate.

Table 3. Vibrational modes (ω) for Neutral, Cation, and Anion of Trans Conformer of Ethyl Formate at the MP2/TZVP Level of Theory in Gas Phase and H$_2$O Ice[a]

mode	vibrational frequencies (cm^{-1})				
	neutral in H$_2$O ice	neutral ω (I)	expt[b] ω (I)	cation ω (I)	anion ω (I)
CH$_2$ asym stretch	3047(28)	3051(27)	—	3081(0.2)	3013(55)
CH$_3$ asym stretch	3037(17)	3039(17.2)	2998(s)	3049(1.3)	2992(65)
CH$_2$ asym.stretch	3015(6)	3020(7.2)	2972(w)	3062(0.1)	2917(52)
C—H stretching	2950(18)	2974(46)	2930(s)	2989(32.9)	2663(501)
CH$_2$ sym stretch	2962(10)	2968(21)	2937(w)	2988(19.2)	2817(123)
CH$_3$ sym stretch	2948(12)	2952(13.1)	2903(w)	2962(1.5)	2913(53)
C=O stretch	1692(498)	1698(293)	1750(vs)	1570(328)	1408(229)
CH$_2$ scissor	1466(14)	1471(9)	—	1454(16)	1476(3.5)
CH$_2$ scissor	1446(2.7)	1454(2.8)	1485(m)	1443(12)	1449(0.8)
CH$_3$ asym deform	1427(8)	1434(6)	1453(m)	1426(13)	1423(1.3)
CH$_3$ sym deform	—	1389(18.5)	1441(w)	1351(48)	—
CH$_3$ rock, CH2 wag	1384(21)	1371(3.6)	1366(m)	1369(27)	1356(33)
CH$_2$ wag	1351(2)	1352(2.6)	1404(w)	1326(100)	1330(7.6)
CH$_2$ twist	1254(2)	1256(1.4)	1278(w)	1254(5)	1221(0.9)
C—O stretch	1146(638)	1172(431)	1191(vs)	1152(33.2)	1116(89)
CH$_2$ rock	1143(7)	1148(4)	1160(s)	1130(11)	1151(2.4)
CH$_3$ rock and CC stretch	1099(11)	1102(6)	1103(s)	—	1116(89)
C—C stretch	1007(28)	1009(15)	1007(m)	1099(5)	1059(89)
H out of O=C—O plane	993(0.04)	994(0.001)	1091(s)	935(41)	1007(3)
CO stretch and CH$_3$ rock	838(25)	837(14)	843(s)	715(84)	876(48)
CH$_2$ and CH$_3$ rocking	794(0.7)	791(0.14)	787(w)	794(2)	782(0.3)
O=C—C and C—O stretch	752(4)	760(2)	758(w)	596(3)	704(218)
OCC scissor	372(7)	368(5)	378 (m)	371(26)	343(1.3)
CH$_3$ rock	216(8)	230(2)	—	225(3)	263(1.5)

[a] Values in parentheses are IR intensities I (km mol^{-1}). [b] Experimental data taken from Peng et al.:[29] (—) not observed; (s) strong; (w) weak; (m) medium; (v) very.

3.2. Infrared Spectra. *3.2.1. IR Spectra of Trans Conformer of Neutral Ethyl Formate and Its Ions.*

The vibrational frequencies of trans and gauche conformers of ethyl formate, their ions and in H$_2$O ice along with experimental values are summarized in Table 3 and Table 4, respectively. For both the conformers of neutral ethyl formate, vibrational frequencies obtained from this work at MP2/TZVP level are in excellent agreement with the experimental values.[29] There are two strongest modes observed experimentally in neutral trans conformer of ethyl formate at 1191 and 1750 cm^{-1} which correspond to the C—O stretch and C=O stretch. Our theoretical spectrum here also shows that these modes are the first and second intense modes in neutral trans conformer which appear at 1172 and 1698 cm^{-1}, respectively. Apart from these two modes other strong modes observed experimentally are at 2998, 2930, 1160, 1103, 1091, and 843 cm^{-1}, which correspond to the CH$_3$ asymmetric stretching, CH stretching, CH$_2$ rock, CH$_3$ rock and CC stretching, H out of O=C—O plane and C—O stretching, and CH$_3$ rock, respectively.

Infrared spectra of neutral trans conformer of ethyl formate and its ions are shown in Figure 2. As can be seen from Table 3 in the theoretical vibrational spectra, apart from the most intense mode, the C—O stretching mode, features at 3051, 3039, 2974, 2968, 1698, 1389, and 1009 cm^{-1} are also intense which correspond to the CH$_2$ asymmetric stretch, CH$_3$ asymmetric stretch, C—H stretch, CH$_2$ symmetric stretch, C=O stretch, CH$_3$ symmetric deformation, and C—C stretching mode. The C—C stretching mode appearing at 1009 cm^{-1} from this work is in excellent agreement with experimental determination of 1007 cm^{-1}.

Large change is observed in the infrared spectra upon ionization of the trans conformer of ethyl formate. The most intense mode, the C—O stretch, in neutral trans ethyl formate does not remain the most intense in its cation and anion. In cation the C=O stretching mode at 1570 cm^{-1} and in anion the C—H stretching mode at 2663 cm^{-1} are the most intense modes. The former is red-shifted by 128 cm^{-1}, whereas the latter by 311 cm^{-1} than the neutral. The second intense mode in cation is the CH$_2$ wagging mode which is of very weak intensity in neutral trans conformer. This mode is red-shifted by 26 cm^{-1} in cation than the neutral. Apart from these two intense modes in cation, features at 2989, 2988, 1454, 1351, 1369, 1152, 715, 935, and 371 cm^{-1} are also intense which correspond to the C—H stretch, CH$_2$ symmetric stretch, CH$_2$ scissor, CH$_3$ symmetric deformation, CH$_3$ rock and CH$_2$ wag, C—O stretch, CO stretch and CH$_3$ rock, H out of plane bending to O=C—O plane, and O—C—O scissor. Out of these modes, the CH$_2$ symmetric and C—H stretching modes are blue-shifted by 20 and 15 cm^{-1}, respectively, than the neutral. On the other hand the CH$_3$ symmetric deformation, C—O stretch, and C—C stretching modes are red-shifted by 38, 20, and 90 cm^{-1}, respectively, than the corresponding mode in neutral trans conformer.
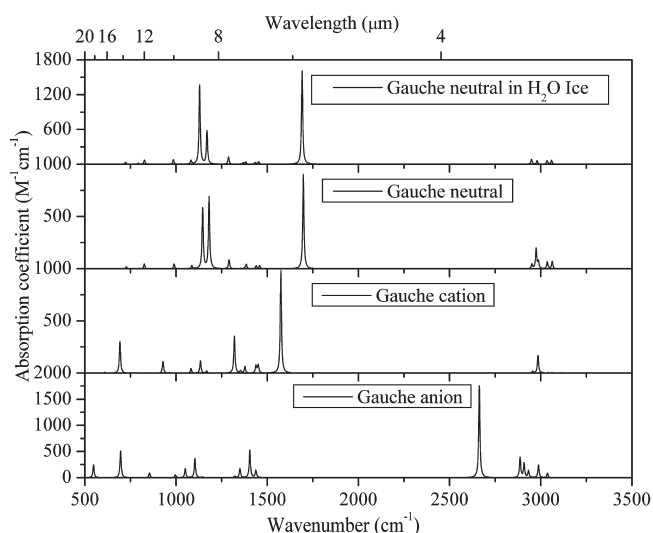
Table 4. Vibrational Modes (ω) for Neutral, Cation, and Anion of Gauche Conformer of Ethyl Formate at the MP2/TZVP Level of Theory in Gas Phase and H$_2$O Ice[a]

mode	vibrational frequencies (cm^{-1})				
	neutral (ice)	neutral (I)	expt[b]	cation (I)	anion (I)
CH$_2$ asym stretch	3059(20)	3062(20)	2998(s)	3109(1.2)	3036(24)
CH$_3$ asym stretch	3040(2)	3018(1.1)	2986(m)	3061(1.9)	2987(70)
CH$_2$ asym stretch	3034(17)	3035(18)	−	3040(1.7)	2932(38)
CH$_2$ sym stretch	2979(18)	2986(19)	2951(w)	3008(0.8)	2886(113)
C−H stretching	2950(10)	2974(56)	2930(s)	2984(50)	2662(519)
CH$_3$ sym stretch	2948(16)	2951(12)	2903(w)	2955(5)	2907(80)
C=O stretch	1691(476)	1698(266)	1750(vs)	1574(290)	1403(154)
CH3 asym deform	1432(8)	1458(8)	1473(m)	1438(20)	1446(3)
CH$_2$ scissor	1438(2)	1446(0.8)	1462(m)	1450(22)	1437(39)
CH$_3$ deformation	1381(12)	1384(12)	1453(m)	1377(18.3)	1321(7.4)
H in plane bend OCO plane	1367(7)	1375(2.8)	−	1319(104)	1259(0.7)
CH$_2$ wag	1352(2)	1354 (1.2)	1404(m)	1352 (6)	1350(50)
CH$_2$ twist	1287(37)	1290(24)	1308(m)	1257(0.6)	1274(0.7)
C−O stretch	1129(401)	1180(202)	1191(vs)	1167(5.8)	1103(107)
CH$_2$ rock	1169(167)	1145(170)	1160(s)	1133(34.8)	1145(3.8)
CH$_3$rock and CC stretch	1081(18)	1086(7)	1103(s)	1081(13)	1050(50)
H out of bend O=C−O plane	1000(0.07)	1000(0.20)	1090(s)	962(1.3)	995(15)
C−C stretch	984(23)	989(13)	995(m)	928(33)	853(25)
CO stretch and CH$_3$ rock	826(21)	825(13)	820(w)	790(1)	771(0.8)
CH$_2$ rock and OC stretch	792(5)	795(1.6)	787(w)	691(88)	695(150)
CH$_2$ rock and OCC deform	722(10)	727(6)	741(m)	609(2)	547(71)
OCC scissor and CO torsion	446(24)	443(15)	455(s)	435(25)	419(6)
COC bend and CC torsion	318(19)	322(12)	320(s)	295(12)	304(5)
CO torsion	214(17)	246(10)	241(m)	−	−
CH$_3$ rock	208(7)	215(2)	−	241(5)	225(4)

[a] Values in parentheses are IR intensities I (km mol^{-1}). [b] Experimental data taken from Peng et al.:[29] (−) not observed; (s) strong; (w) weak; (m) medium; (v) very.
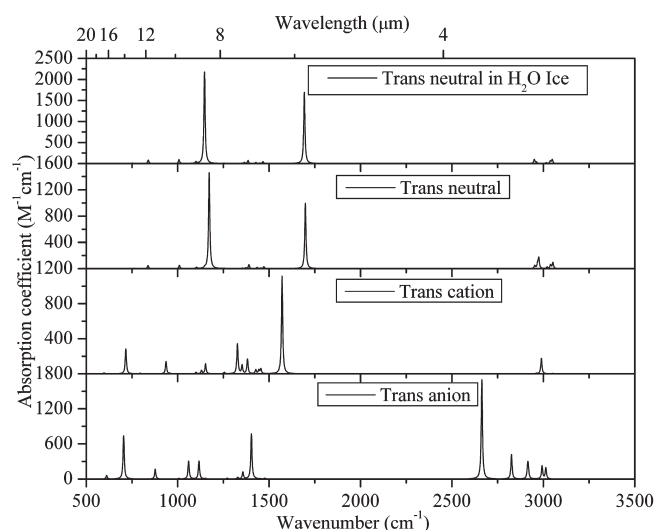
Figure 2. Infrared spectra of the trans conformer of ethyl formate and its ions.

Figure 3. Infrared spectra of the gauche conformer of ethyl formate and its ions.

The infrared spectrum of the anion of the trans conformer is dominated by the C−H stretching mode appearing at 2663 cm^{-1} and is blue-shifted by 311 cm^{-1} in anion than the neutral. The

second intense mode for the anion of the trans conformer is the C=O stretching mode which is also the second intense mode for the neutral trans ethyl formate. The C−O stretching and

C–C stretching modes appearing at 1116 and 1059 cm⁻¹, respectively, are of the same IR intensity in the anion of the trans conformer. The former is red-shifted by 56 cm⁻¹ and the latter blue-shifted by 50 cm⁻¹ in the anion than the neutral. Five other modes, viz., C=O stretch, CH_3 asymmetric stretch, CH_2 asymmetric stretch, CH_3 symmetric stretch, and C–O and O=C–C stretch appearing at 1408, 2992, 2917, 2913, and 704 cm⁻¹, respectively, are also intense. These modes are red-shifted by 290, 47, 103, 39, and 56 cm⁻¹ than the corresponding modes in neutral trans conformer of ethyl formate.

3.2.2. IR Spectra of Gauche Conformer of Neutral Ethyl Formate and Its Ions. The vibrational modes of the gauche conformer of ethyl formate, its ions, and that in H_2O ice with the available experimental values are summarized in Table 4. Similar to trans conformer, the C=O stretching and C–O stretching modes are very strong modes in gauche conformer appearing at 1750 and 1191 cm⁻¹, which are in agreement with the calculated modes at 1698 and 1180 cm⁻¹, respectively.[29] Figure 3 shows infrared spectra of neutral and charged gauche conformer of ethyl formate. The most intense mode in the neutral gauche conformer is the C=O stretching mode appearing at 1698 cm⁻¹. This mode was the second intense mode in neutral trans conformer of ethyl formate. The second intense mode for the neutral gauche conformer is the C–O stretching mode appearing at 1180 cm⁻¹ which was the most intense in neutral trans conformer. This C=O stretching mode is also observed to be the most intense experimentally.[29] Other modes appeared at 1145, 2974, 2986, 3062, and 1290 cm⁻¹ are also intense which correspond to the CH_2 rock, C–H stretching, CH_2 symmetric stretch, CH_2 asymmetric stretch, and CH_2 twist, respectively.

Similar to neutral gauche conformer, the dominant mode in the infrared spectrum of its cation is the C=O stretching mode appearing at 1574 cm⁻¹ and is red-shifted by 124 cm⁻¹ in the cation than the neutral. The CH_3 asymmetric stretch, CH_2 symmetric stretch, CH_2 twist, C–O stretch, and CH_2 rock modes, which are of significant IR intensity in neutral gauche conformer, become less intense in cation than the neutral. The hydrogen in plane vibration with the O=C–O plane is the second intense mode in the cation, which was less IR active in the neutral. This mode is red-shifted by 56 cm⁻¹ in the cation than the neutral. Apart from these two intense modes in the cation, other intense modes are the CH_2 scissor, CH_2 rock, C–C stretch, and C–H stretching modes appearing at 1450, 1133, 928, and 2984 cm⁻¹, respectively. These modes are blue-, red-, red-, and blue-shifted, respectively, than the corresponding modes in neutral gauche conformer.

The most intense mode, the C=O stretch, in the neutral and cation of the gauche conformer does not remain the most intense in the anion and is observed at 1403 cm⁻¹ in the anion of the gauche conformer. But this mode is of significant IR intensity and blue-shifted by 295 cm⁻¹ in the anion than the neutral. Similar to the anion of the trans conformer, in the infrared spectrum of the anion of the gauche conformer, the C–H stretching mode is dominant and red-shifted by 312 cm⁻¹ than the neutral. The CH_2 wag, CH_2 symmetric stretch, and C–O stretching modes appearing at 1350, 2886, and 1103 cm⁻¹, respectively, are also quite intense. The CH_2 wag and CH_2 symmetric stretching modes are blue-shifted by 4 and 103 cm⁻¹, respectively, whereas the C–O stretching mode is red-shifted by 77 cm⁻¹. Apart from these, features at 1437, 2907, 2987, and 2932 cm⁻¹ are also of significant intensity, which correspond to the CH_2 scissor, CH_3 symmetric stretch, CH_3 asymmetric, and CH_2 asymmetric
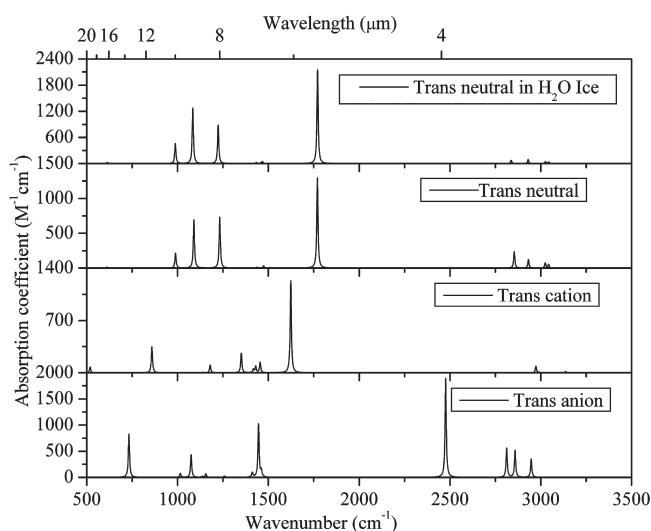

Figure 4. Infrared spectra of trans conformer of methyl formate and its ions.

stretching, respectively. These modes are red-shifted in the anion by 9, 44, 31, and 103 cm⁻¹, respectively, than the neutral. The highest red-shifted mode is the CH_2 asymmetric stretching mode. The CH_2 asymmetric stretch, CH_3 asymmetric stretch, CH_2 symmetric stretch, CH_2 wag, and C–H stretching modes which were less intense in the neutral become more intense in the anion of the gauche conformer.

3.2.3. Neutral Ethyl Formate in Gas Phase and H_2O Ice. We now compare the vibrational spectra of neutral ethyl formate in gas phase and in astrophysical H_2O ice. The most intense mode in the neutral trans conformer of ethyl formate in gas phase as well as in H_2O ice is the C–O stretching mode. This mode is observed at 1172 cm⁻¹ in the gas phase and blue-shifted by 26 cm⁻¹ in H_2O ice. It is more intense in H_2O ice than that in the gas phase. The second intense mode in gas phase is the C=O stretching mode which appears at 1698 cm⁻¹ and blue-shifted by 8 cm⁻¹ in H_2O ice than the gas phase. A change in IR intensity in H_2O ice than the gas phase is observed for the modes CH stretching, CH_3 rock and CH_2 wag, and C–C stretching modes. A blue shift of 24, 13, and 2 cm⁻¹, respectively, is observed for these modes in H_2O ice than the gas phase. The CH_3 symmetric deformation mode which is the fifth intense mode in the gas phase is absent in H_2O ice.

The most intense mode for gauche conformer in the gas phase as well as H_2O ice is the C=O stretching mode which is blue-shifted by 7 cm⁻¹ in H_2O ice than in the gas phase. This mode is more intense in H_2O ice than the gas phase. The C–O stretch, CO torsion, and CH_3 asymmetric deformation modes are blue-shifted in H_2O ice by 51, 32, and 26 cm⁻¹, respectively, than in the gas phase. The first and second intense modes, the C=O stretching and C–O stretching modes, are about twice as intense in H_2O ice than in the gas phase, and the third intense mode the CH_2 rock is of almost same IR intensity in gas phase and in H_2O ice. The CH_2 rock mode is red-shifted by 24 cm⁻¹ in H_2O ice than the gas phase.

3.2.4. Infrared Spectra of Trans Conformer of Methyl Formate and Its Ions. The vibrational spectra of neutral, cation, and anion of the trans conformer of methyl formate in the gas phase and the neural trans conformer in astrophysical H_2O ice are shown in Figure 4, and vibrational modes are represented in

Table 5. Vibrational Modes (ω) for Neutral, Cation, and Anion of Trans Conformer of Methyl Formate at the MP2/TZVP Level of Theory in Gas Phase and H_2O Ice[a]

mode	vibrational frequencies (cm^{-1})			
	neutral in H_2O ice	neutral ω (I)	cation ω (I)	anion ω (I)
CH_2 asym stretch	3042(11)	3043(15)	3136(5)	2946(103)
CH_3 asym stretch	3025(14)	3024(22)	3118(1)	2858(152)
CH_3 sym stretch	2930(27)	2931(36)	2990(2)	2811(165)
CH stretch	2837(22)	2854(70)	2972(26)	2475(558)
C=O stretch	1770(635)	1770(383)	1622(362)	1445(300)
CH_2 scissor	1467(15)	1473(9)	1454(41)	1461(35)
CH_3 sym deform	1458(4)	1452(1.8)	1430(25)	1411(25)
CH_3 asym deform	1433(8)	1436(3.6)	1417(14)	1401(1.8)
H in plane bend to OCO	1399(1)	1385(2.4)	1179(30)	1258(7)
CH_3 rock and CO stretch	1223(261)	1232(216)	1146(1.2)	1155(19)
CH_2 rock	1154(1)	1149(0.7)	1135(1)	1136(5)
CH_3 rock and COC torsion	1083(375)	1090(205)	1134(26)	---
H out of plane bend to OCO	1007(0)	997(0.2)	973(0.9)	1015(21)
C—O stretch	987(135)	988(63)	858(102)	732(244)
O=C—O stretch	604(8)	610(4)	518(23)	473(18)

[a] Values in parentheses are IR intensities I ($km\ mol^{-1}$).

Table 6. Vibrational Modes (ω) for Neutral, Cation, and Anion of Cis Conformer of Methyl Formate at the MP2/TZVP Level of Theory in Gas Phase and H_2O Ice[a]

mode	vibrational frequencies (cm^{-1})				
	neutral in H_2O ice	neutral ω (I)	expt[b] ω	cation ω (I)	anion ω (I)
CH_3 asym stretch	3126(2)	3090(10)	3045	3144(6)	2918(106)
CH_2 asym stretch	3093(3)	3054(17)	—	3103(1)	2957(77)
CH_3 sym stretch	2977(8)	2964(28)	2969	2985(0.7)	2836(156)
CH stretch	2948(6)	2981(42)	2943	2994(56)	2658(512)
C=O stretch	1602(743)	1701(279)	1754	1581(307)	—
CH_2 scissor	1432(7)	1455(10)	—	1426(8)	1461(4)
CH_3 asym deform	1428(12)	1438(7)	1454	1439(24)	1425(104)
CH_3 sym deform	1383(80)	1435(2)	1445	1412(58)	1409(1)
H in plane bend to OCO	1323(116)	1371(1)	1371	1334(62)	1270(2)
OCO stretch	1298(115)	1199(207)	1213	1134(8)	—
CH_3 rock	1141(3)	1153(136)	1166	1183(11)	1157(2)
CH_2 rock	1124(4)	1146(2)	—	1131(5)	1136(1)
H out of plane to OCO	984(0.8)	993(0)	1032	954(1)	989(14)
C—O stretch	785(83)	914(28)	938	788(72)	719(166)
OCO stretch	746(0.1)	748(8)	767	610(8)	557(44)
CH_2 rock and COC torsion	298(45)	326(28)	318	360(40)	320(7)
CH_3 torsion	166.2(0.01)	153.4(0.1)	130	75(0.2)	150(3.8)

[a] Values in parentheses are IR intensities I ($km\ mol^{-1}$). [b] Experimental data taken from a reference by Chao et al. in ref 41.

Table 5. The most intense mode for neutral trans conformer in the gas phase is the C=O stretching mode which is observed at 1770 cm^{-1}. The CH_3 rock and C—O stretching modes are the second intense modes, and CH_3 rock and COC torsion are the third intense modes which are observed at 1232 and 1090 cm^{-1}, respectively. Apart from these modes other modes of significant intensity appeared at 2854, 988, and 2931 cm^{-1}, which correspond to the CH stretch, C—O stretch, and CH_3 symmetric stretch.

Upon ionization, significant change is observed in vibrational frequencies and IR intensities. The C=O stretching is the most

intense mode in the trans conformer of neutral methyl formate which remains the most intense mode in its cation and becomes the second most intense in its anion. This mode is red-shifted by 148 cm^{-1} in cation than in the neutral with almost the same IR intensity. The second most intense modes, the CH_3 rock and C—O stretch in the neutral trans conformer, do not remain the second most intense modes in the cation and anion and are blue-shifted by 86 and 77 cm^{-1} in cation and anion, respectively. However these modes are of negligible IR intensity in cation and anion as compared to the neutral. The third most intense modes
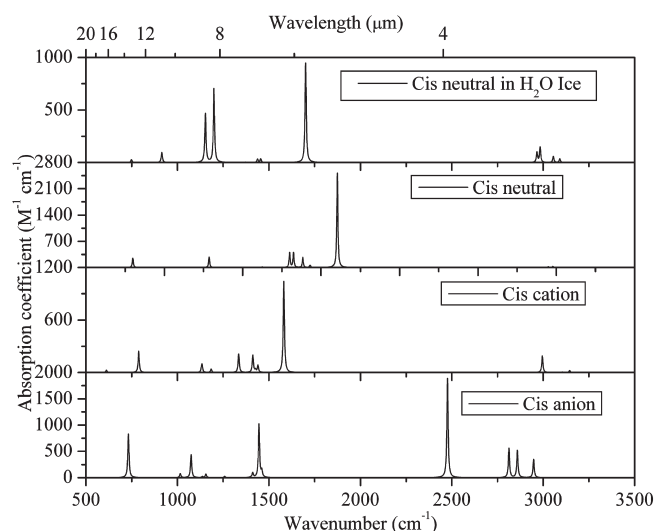
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Figure 5. Infrared spectra of cis conformer of methyl formate and its ions.

in the neutral trans conformer of methyl formate, the CH_3 rock and COC torsion, become eight times less intense in the cation and absent in the anion. The second and third most intense modes in the cation are the C—O stretch and CH_2 scissor, respectively, appearing at 858 and 1454 cm^{-1}. Apart from these modes, the cation has other intense modes observed at 1179, 2972, 1134, and 1430 cm^{-1} which correspond to the H in plane bending to the OCO plane, CH stretch, CH_3 rock and COC torsion, and CH_3 symmetric deformation.

The CH stretch is the most intense mode in the anion of the trans conformer of methyl formate which is observed at 2475 cm^{-1}. This mode is very weak in the neutral and cation as compared to the anion. It is the fourth and fifth most intense modes in the neutral and cation, respectively. A large blue shift of 379 cm^{-1} for this mode is observed in the anion than in the neutral. The second most intense mode in the anion is the C=O stretch, which is the first most intense mode in the neutral and cation. This mode is observed at 1445 cm^{-1} and blue-shifted by 325 cm^{-1} in the anion than in the neutral with less IR intensity in the anion than in the neutral. The third most intense mode, the C—O—C stretch, is observed at 732 cm^{-1}. The CH_3 symmetric stretching, CH_3 asymmetric stretching, and CH_2 asymmetric stretching modes appearing at 2811, 2858, and 2946 cm^{-1} are four, seven, and seven times more intense than the corresponding modes in the neutral. These modes are blue-shifted by 120, 166, and 97 cm^{-1} in the anion than in the neutral. Almost all of the modes in the anion are intense except the CH_3 asymmetric deformation, H in plane bending to OCO plane, and CH_2 rock which appeared at 1401, 1258, and 1136 cm^{-1}, respectively.

3.2.5. Infrared Spectra of Cis Conformer of Methyl Formate and Its Ions. The cis conformer of methyl formate is more stable than its trans conformer. The vibrational modes of the neutral, cation, and anion of the trans conformer of methyl formate in the gas phase with the available experimental values[40] and the neutral cis conformer in H_2O ice are summarized in Table 6, and corresponding spectra are shown in Figure 5. The most intense mode in the neutral cis conformer in the gas phase is the C=O stretching mode which is observed at 1701 cm^{-1}. This mode is also the most intense mode in its cation and absent in the anion. The second most intense mode in neutral cis conformer in the

gas phase is the O—C—O stretch, which is observed at 1199 cm^{-1} and is in good agreement with the experimental value of 1213 cm^{-1}. This mode is of negligible intensity in the cation and blue-shifted by 65 cm^{-1}, whereas this mode is absent in the anion. The third most intense mode is the CH_3 rock mode which appears at 1153 cm^{-1} and is in close agreement with the experimental value of 1166 cm^{-1}. Methyl formate has already been detected in interstellar medium using its torsional mode in ground and excited states in Orion KL.[45] The CH_3 torsion mode of the neutral cis conformer is obtained at 153 cm^{-1}. The CH stretch, C—O stretch, and CH_3 asymmetric stretch observed at 2981, 914, and 2964 cm^{-1} are also intense. Three vibrational modes, the CH_3 symmetric stretch, CH_2 rock and C—O—C torsion, C—O stretch modes, are of the same IR intensity in the neutral cis conformer of methyl formate in the gas phase.

Similar to the neutral cis conformer in the gas phase, the most intense mode in its cation is the C=O stretch which is blue-shifted by 120 cm^{-1} in the cation than in the neutral. The C—O stretching mode is the second most intense mode in the cation, and the second most intense mode in the neutral, the O—C—O stretch, is of negligible intensity in the cation. The third most intense mode in the cation is the H in plane bending to the OCO plane, which is observed at 1334 cm^{-1} and is blue-shifted by 37 cm^{-1} than in the neutral. It is 60 times more intense in the cation than the neutral. The most intense mode in the neutral and cation, the C=O stretch, is absent in the anion. In the anion the most intense mode is the CH stretching mode, which appeared at 2658 cm^{-1} and is about 12 times more intense in the anion than the neutral. The second most intense mode in the anion is the CH_3 symmetric stretching mode appearing at 2836 cm^{-1} and is five times more intense than that of the neutral. This mode is blue-shifted by 128 cm^{-1} in the anion than in the neutral. Other intense modes in the anion are the CH_3 asymmetric stretch, CH_3 asymmetric deformation, and CH_2 asymmetric stretch, which appeared at 2918, 1425, and 2957 cm^{-1}, respectively. These modes are blue-shifted in the anion than in the neutral by 172, 13, and 97 cm^{-1}, respectively.

3.2.6. Methyl Formate in Gas Phase and H_2O Ice. As observed for the gas phase, the most intense mode for neutral methyl formate in H_2O ice is also the C=O stretching mode, which appeared at 1770 cm^{-1}. However its intensity in H_2O ice is about twice that in the gas phase. The second most intense modes in H_2O ice are the CH_3 rock and COC torsion observed at 1083 cm^{-1}, which are the third most intense modes for neutral trans methyl formate in the gas phase. However, these modes are more intense in H_2O ice than the the gas phase. The third most intense modes in H_2O ice are the CH_3 rock and C—O stretch observed at 1223 cm^{-1}, which are the second most intense modes for neutral trans methyl formate in the gas phase. These modes are blue-shifted by 9 cm^{-1} in H_2O ice than in the gas phase and are more intense in the former than in the latter. The C—O stretching mode is about twice as intense in H_2O ice as in the neutral. On the other hand the C—H stretching mode in H_2O ice is three times less intense than that for the gas phase and blue-shifted by 17 cm^{-1} in H_2O ice.

The most intense mode for the cis conformer in the gas phase, the C=O stretch, is also the most intense mode in H_2O ice. However, this mode is about three times more intense in H_2O ice than in the gas phase and blue-shifted by 101 cm^{-1} in H_2O ice than in the gas phase. There are two modes, the O—C—O stretch and H in plane bending to O—C—O plane, which are of the same IR intensity and are the second most intense modes in H_2O ice.

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Table 7. Rotational and Centrifugal Distortion Constants of Neutral Conformers of Ethyl Formate at the MP2/TZVP Level of Theory with the Available Experimental Results

	trans				gauche			
constant	neutral H$_2$O ice	neutral	expt[a]	expt[b]	neutral H$_2$O ice	neutral	expt[a]	expt[b]
A (MHz)	17782	17782	17746	17746	9855	9855.9	9985.5	9985.6
B (MHz)	2909	2909	2904.7	2904.7	3893	3893.2	3839.6	3839.6
C (MHz)	2580	2580	2579.1	2579.1	3230	3230.4	3212.8	3212.8
Δ_J (kHz)	0.58	0.604	0.6243	0.6232	4.125	5.4126	5.939	5.9493
Δ_{JK} (kHz)	−3.14	−2.68	−3.486	−3.543	−17.32	−25.31	−32.33	−32.37
Δ_K (kHz)	42.9	43.93	51.353	81.80	42.24	57.71	78.75	85.81
δ_J (kHz)	0.095	0.100	0.1017	0.101	1.31	1.856	2.001	2.000
δ_K (kHz)	0.023	−1.44	−0.985	−0.88	6.03	7.545	7.177	7.431
Φ_J (mHz)	0.03	−0.06	−	−	−14.1	−51	−53	−55
Φ_{JK} (mHz)	0.42	−1.97	−	−	179	517	916	769
Φ_{JK} (Hz)	0.005	−0.01	−0.024	−	−0.062	−0.204	−0.074	−
Φ_{KJ} (Hz)	−0.36	−0.94	−0.833	−1.13	−0.836	−2.062	−4.156	−3.66
Φ_j (mHz)	0.03	−0.01	−	−	−6.3	−2.2	−2.6	−
Φ_k (Hz)	0.613	1.127	0.209	−	1.459	3.559	7.650	−
Φ_k (Hz)	0.721	1.109	−	−	0.29	0.0398	1.785	−

[a] Experimental data taken from Medvedev et al. in ref 32. [b] Experimental data tacken from Demaison et al. in ref 33.

The O−C−O stretch is observed at 1298 cm^{-1} in H$_2$O ice and red-shifted by 100 cm^{-1} in H$_2$O ice than the the gas phase. The CH$_3$ torsion mode in the gas phase and H$_2$O ice differ by 13 cm^{-1}. The CH$_3$ symmetric deformation mode is of negligible IR intensity in neutral cis methyl formate in the gas phase, and it becomes the fourth most intense mode in H$_2$O ice. On the other hand the CH$_3$ rock mode, which was the third most intense mode in the gas phase, is of negligible IR intensity in H$_2$O ice.

3.2.7. Comparison of Trans Conformers of Ethyl and Methyl Formate. We now compare the vibrational spectra of the neutral trans conformer of ethyl and methyl formate in the gas phase. All of the vibrational modes for methyl formate are also observed for ethyl formate except the H in plane bend to O−C=O plane mode. This mode appeared at 1385 cm^{-1} in methyl formate. The most intense peak in ethyl and methyl formate is different. It is the C=O stretch and C−O stretch in methyl and ethyl formate, respectively. The most intense peak in methyl formate appeared at 1770 cm^{-1} and that in ethyl formate at 1172 cm^{-1}. The first intense mode in methyl formate is the second most intense in ethyl formate, and the first most intense mode in ethyl formate is the fifth most intense mode in methyl formate. The most intense mode in methyl fomate, the C=O stretching mode, is blue-shifted by 72 cm^{-1} in ethyl formate than in methyl formate. The second most intense mode in ethyl and methyl formate is also different. It is the C=O stretch in the former and the CH$_3$ rock for the latter. The C−H stretching mode, the third and fourth most intense in ethyl and methyl formate, respectively, is more intense in methyl formate than in ethyl formate. It is red-shifted by 120 cm^{-1} in ethyl formate than in methyl formate.

The rotational and distortion constants for neutral trans and gauche conformers of ethyl formate at the MP2/TZVP level of theory with the available experimental constants are summarized in Table 7. The calculated constants are in good agreement with the available experimental values.[32,33] The rotational and distortion constants of neutral trans and cis conformers of methyl formate at the MP2/TZVP level of theory with the available

experimental values for the cis conformer are summarized in Table 8.

3.3. Electronic Absorption Spectra. *3.3.1. Electronic Absorption Spectra of Trans Conformer of Ethyl Formate.* The electronic absorption spectra of the trans conformer of the neutral, cation, and anion in the gas phase and the neutral conformer of ethyl formate in H$_2$O ice are shown in Figure 6. The electronic states of the trans and gauche conformer of the neutral, cation, and anion are ^{1}A, ^{2}A, and ^{2}A, respectively. The electronic absorption spectrum of the neutral trans conformer in H$_2$O ice is characterized by seven intense peaks at 51.8, 60.4, 73.3, 82, 87.8, 98.2, and 130 nm with the major contribution from H−4→L+13, H−3→L+11, H→L+12, H−4→L+1, H−2→L+3, H−2→L+1, and H→L respectively. Here H and L represent the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), respectively. The HOMO−LUMO gap for the neutral trans conformer in H$_2$O ice is 387 kcal mol^{-1}. The first five transitions are in the vacuum-UV and the remaining two in the far-UV regions. All of these transitions are $\sigma \rightarrow \sigma^*$ transitions.
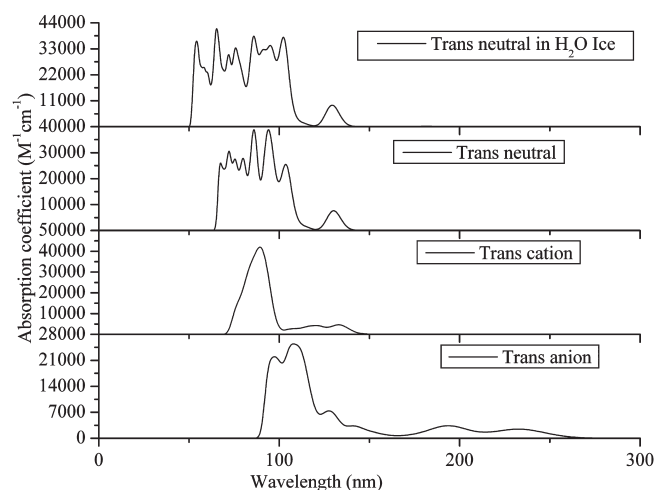
The electronic absorption spectrum of the neutral trans conformer in the gas phase is also characterized by seven intense peaks. Out of these seven transitions, the first five transitions are in the vacuum-UV and the remaining two in the far-UV regions. All of these transitions at 67.1, 72.3, 78.5, 86.7, 96.2, 103.3, and 130.1 nm were assigned to $\sigma \rightarrow \sigma^*$ transitions with the major contribution from H−3→L+14, H−5→L+6, H−3→L+9, H−1→L+6, H−1→L+5, H−2→L, and H−1→L+1, respectively. The HOMO−LUMO gap in the neutral trans conformer is found to be 202.9 kcal mol^{-1}.

The electronic absorption spectrum of the cation of the trans conformer is characterized by four peaks. All of these four transitions at 84.2, 90.4, 121.6, and 132.7 nm were assigned to the $\sigma \rightarrow \sigma^*$ transition with ^{2}A transition symmetry. The major contribution for these four transitions is from H−3→L+4, H−1→L+1, H−1→L, and H−4→L transitions, respectively. The first two transitions are in the vacuum-UV and remaining

Table 8. Rotational and Centrifugal Distortion Constants of Neutral Conformers of Methyl Formate at the MP2/TZVP Level of Theory with the Available Experimental Results
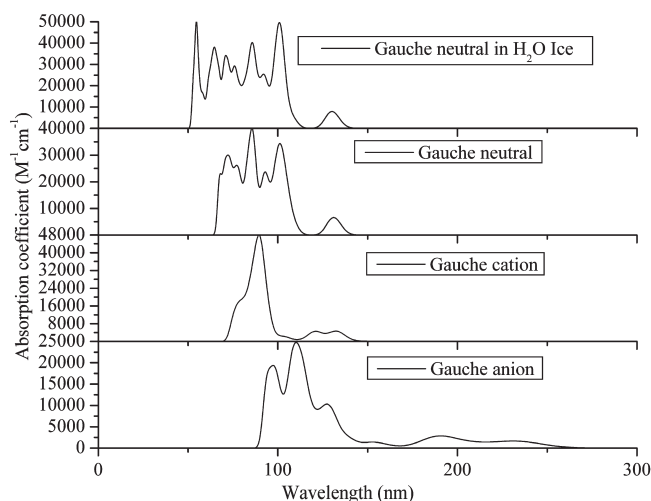
	trans		cis			
constant	neutral H_2O ice	neutral gas	neutral gas	neutral H_2O ice	expt[a]	expt[b]
A (MHz)	48677	48677	19602	19901	19985.7	19980.3
B (MHz)	4650	4650	6756	6930	6914.7	6913.6
C (MHz)	4362	4362	5195	5312	5304.4	5304.5
Δ_J (kHz)	0.922	0.924	5.361	5.872	6.1781	5.885
Δ_{JK} (kHz)	5.507	7.99	−20.08	−21.9	−17.19	−23.31
Δ_K (kHz)	413.8	405.9	77.71	73.24	82.35	75.40
δ_J (kHz)	0.082	0.081	1.649	1.822	1.9502	1.857
δ_K (kHz)	−53.66	−50.00	5.285	5.187	7.66	2.057
Φ_J (mHz)	0.016	0.062	−18.34	−20.88	−	−
Φ_{JK} (Hz)	−0.425	−0.352	0.0463	0.093	−	−
Φ_{JK} (Hz)	−0.271	−0.377	−0.112	−0.084	−	−
Φ_{KJ} (Hz)	−16.16	−23.37	−0.241	−0.514	−	−
Φ_k (Hz)	21.2	28.84	0.1551	1.084	−	−
Φ_k (Hz)	−47.3	−43.41	0.6003	0.232	−	−
Φ_j (mHz)	0.047	0.043	−8.457	−9.492	−	−

[a] Experimental data taken from Plummer et al.[39]. [b] Experimental data taken from Plummer et al.[40]

Figure 6. Electronic absorption spectra of trans conformer of ethyl formate and its ions.

Figure 7. Electronic absorption spectra of gauche conformer of ethyl formate and its ions.

two in the far-UV regions. The HOMO−LUMO gap in the cation of the trans conformer is 359.6 kcal mol^{-1}. The first absorption peak appeared at 67.1 nm in the neutral trans conformer, whereas in the cation it appeared at 84.2 nm. Thus, there is a bathochromic shift of 17.1 nm for the first peak. The last absorption peak appeared at 130.1 nm in the neutral trans conformer, whereas in the cation it appeared at 132.7 nm, indicating a bathochromic shift of 2.6 nm in the last peak in the cation than in the neutral.

There are five absorption peaks in an absorption spectrum of the anion of the trans conformer which appeared at 97.6, 106.5, 127.2, 190, and 235.4 nm with ^2A transition symmetry. The major contribution for these five transitions is from H→L+14, H−6→L−1, H−2→L+5, H→L+1, and H→L+4, respectively. These five transitions are $\sigma \rightarrow \sigma^*$ transitions. The first transition is in the vacuum-UV and remaining four are in the far-UV regions.

The first and last absorption peaks in the anion are shifted to longer wavelength than the neutral. The bathochromic shift of 30.5 and 105.3 nm is observed in the first and last absorption peaks, respectively, of the anion of the trans conformer than the the neutral. A large HOMO−LUMO gap of 212.2 kcal mol^{-1} is observed for the anion of the trans conformer.

3.3.2. Electronic Absorption Spectra of Gauche Conformer of Ethyl Formate. Figure 7 shows electronic absorption spectra of the neutral gauche conformer of ethyl formate in the gas phase and H_2O ice and its ions in the gas phase. Similar to the absorption spectrum of the neutral trans conformer, the absorption spectrum of the neutral gauche conformer is also characterized by seven peaks. All of these seven transitions are the $\sigma \rightarrow \sigma^*$ transition with ^1A transition symmetry. The first five transitions are in the vacuum-UV and the remaining two in the far-UV regions. These peaks are observed at 67.6, 70, 74, 86.4, 93, 101.8,
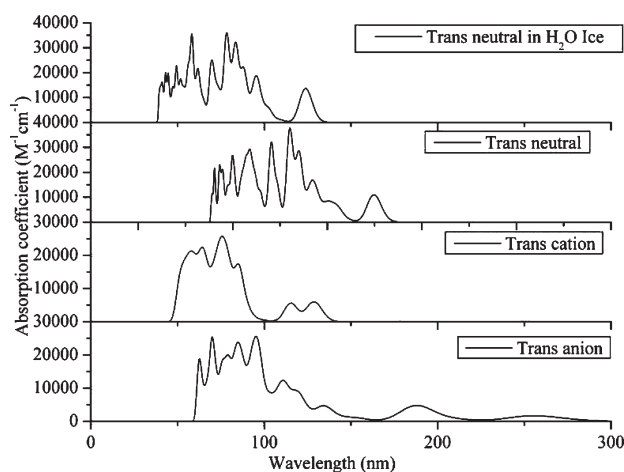
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Figure 8. Electronic absorption spectra of trans conformer of methyl formate and its ions.

Figure 9. Electronic absorption spectra of cis conformer of methyl formate and its ions.

and 131 nm with major contributions from H−1→L+16, H−6-→L+3, H−6→L+6, H−1→L+8, H−2→L+4, H−1→L+3, and H−1→L+1 transitions, respectively. The HOMO−LUMO gap in the neutral gauche conformer of ethyl formate is 380.5 kcal mol^{-1}.

The electronic absorption spectrum of the cation of the gauche conformer has five strong peaks. All three transitions are $\sigma \rightarrow \sigma^*$ transitions with transition symmetry of ^{2}A. These transitions occur at 77, 81.18, 90.33, 119.7, and 132.5 nm with major contributions from H−3→L+7, H−3→L+6, H−1→L+4, H−4→L−1, and H−5→L transitions, respectively. The HOMO−LUMO gap in the cation of the gauche conformer of ethyl formate is 366.6 kcal mol^{-1}. The first three transitions are in the vacuum-UV and the remaining two in the far-UV regions. The bathochromic shift of 9.4 and 1.5 nm is observed in the first and last peaks, respectively, in the absorption spectrum of the cation.

The electronic absorption spectrum of the anion of the gauche conformer shows five intense peaks in the UV and far-UV regions. These five peaks appear at 97.6, 107.2, 123.5, 189.4, and 234.7 nm with major contributions from H−4→L+1, H−5→L−1, H−3→L+2, H→L+1, and H→L+4 transitions, respectively. The first transition is in the vacuum-UV and the remaining four in the far-UV regions. The transition symmetry is ^{2}A, and the nature of the transitions is $\sigma \rightarrow \sigma^*$ electronic transition. The HOMO−LUMO gap in the anion of the gauche conformer is 224.4 kcal mol^{-1}. The HOMO to LUMO transition is the $\sigma \rightarrow \sigma^*$ transition. For the anion of the gauche conformer, bathochromic shifts of 30 and 103.7 nm are observed for the first and last peaks, respectively, in the absorption spectrum.

3.3.3. Electronic Absorption Spectra of Trans Conformer of Methyl Formate. The electronic absorption of the spectra of the neutral, cation, and anion of the trans conformer of methyl formate in the gas phase and the neutral in H_2O ice are shown in Figure 8. The electronic absorption spectra of the trans conformer in H_2O ice is characterized by seven intense peaks. All of these seven transitions show $\sigma \rightarrow \sigma^*$ with transition symmetry ^{1}A. These peaks are observed at 51.8, 60.4, 64.4, 81.9, 87.5, 99.4, and 129.9 nm with major contributions from H−6→L−+11, H−3→L+11, H−7→L+2, H−4→L+1, H−2→L+3, H−2→L+1, and H→L. The first six transitions are in the vacuum-UV and a remaining one is in the far-UV regions. The
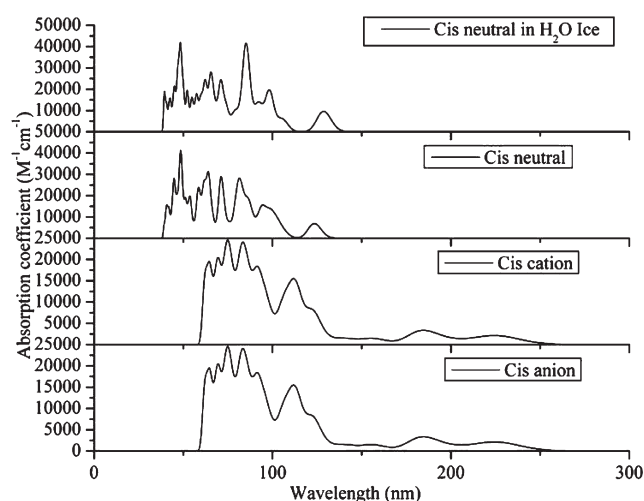
HOMO−LUMO gap for the neutral conformer in the gas phase is 387.4 kcal mol^{-1}. The electronic absorption spectrum of neutral methyl formate in the gas phase is characterized by eight intense peaks. These peaks are observed at 42.7, 45.6, 52.6, 62.6, 74.4, 84.3, 96.7, and 131.2 nm with the major contribution from H→L+25, H−4→L+18, H−1→L+18, H→L+14, H−2→L+7, H−4→L+3, H→L, and H−1→L+1, respectively. The first seven transitions are in the vacuum-UV and a remaining one is in the far-UV regions. The HOMO−LUMO gap for the neutral conformer in H_2O ice is 375.9 kcal mol^{-1}.

The absorption spectrum of the cation of the trans conformer in the gas phase is characterized by eight intense peaks at 53, 57.6, 61.7, 66.7, 77.7, 88.1, 120.8, and 135 nm with the major contribution from H−2→L+13, H−7→L+1, H−4→L+4, H−2→L+9, H−2→L+5, H−7→L+1, H−1→L, and H→L, respectively. The first six transitions are in the vacuum-UV and the remaining two in the far-UV regions with a transition symmetry of ^{2}A. The HOMO− LUMO gap for the cation is 389.7 kcal mol^{-1}. The electronic absorption spectrum of the anion of the trans conformer shows six intense peaks at 65.4, 73.3, 90.1, 101.2, 117, and 194.6 nm with major contributions from H−6→L+7, H−6→L+3, H→L+13, H→L+10, H−2→L+1, and H→L+3, respectively. The HOMO−LUMO gap for the anion of the trans conformer is 219 kcal mol^{-1}. The transition symmetry here is ^{2}A with the first three transitions in the vacuum-UV and those remaining in the far-UV regions.

3.3.4. Electronic Absorption Spectra of Cis Conformer of Methyl Formate. The electronic absorption spectra of the cis conformer of the neutral, cation, and anion of methyl fomate in the gas phase and the neutral in H_2O ice are shown in Figure 9. The absorption spectrum of the neutral cis conformer in H_2O ice shows seven intense peaks out of which the first five are in the vacuum-UV and the remaining two in the far-UV regions. The transition symmetry is ^{1}A, and these transitions are observed at 41.2, 51.2, 69.2, 75.2, 89.6, 103.6, and 135.4 nm with major contributions from H−1→L+26, H−7→L+9, H−2→L+9, H−1→L+10, H−1→L+5, H→L+2, and H−1→L, respectively. The HOMO−LUMO gap for the neutral cis conformer in H_2O ice is 382 kcal mol^{-1}. The neutral cis conformer in the gas phase has eight intense peaks in its absorption spectrum. These peaks are observed at 42.8, 47.6, 51, 61, 67.9, 74.9, 86, and
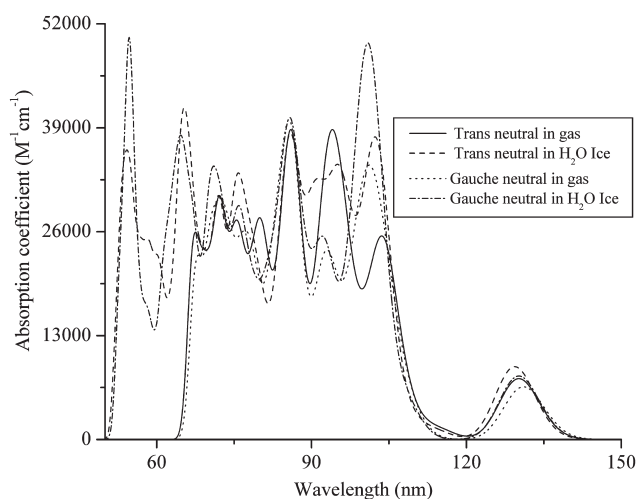
Figure 10. Comparative electronic absorption spectra of neutral trans and gauche conformer of ethyl formate in gas phase and H$_2$O ice.
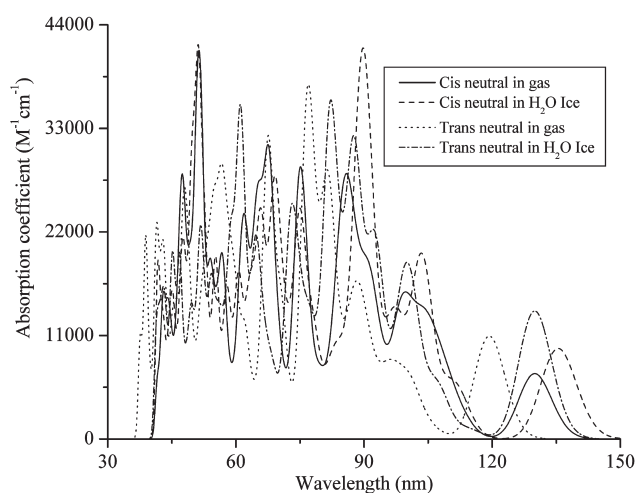

Figure 11. Comparative electronic absorption spectra of neutral trans and cis conformer of methyl formate in gas phase and H$_2$O ice.

130 nm with major contributions from H−1→L+21, H−9-→L+3, H−7→L+10, H→L+13, H−7→L+3, H−4→L+2, H−4→L+3, and H−1→L, respectively. The HOMO−LUMO gap is 394.3 kcal mol^{-1} for the cis conformer of the cation in the gas phase. There are six intense peaks in the absorption spectra for the anion of the cis conformer in the gas phase, out of which the first four are in the vacuum-UV and the remaining two transitions in the far-UV regions. These transitions are observed at 67.6, 73.9, 79, 87.1, 116.5, and 192.4 nm with major contributions from H−5→L+8, H−7→L+4, H−2→L+10, H−4→L+1, H−3→L+1, and H→L+3, respectively. The HOMO−LUMO gap for this anion is 219.7 kcal mol^{-1}.

3.4. Comparison of Electronic Absorption Spectra. Figure 10 shows the comparative electronic absorption spectra of the neutral trans and gauche conformer of ethyl formate in gas and in astrophysical H$_2$O ice. The absorption spectrum of both trans and gauche conformers of ethyl formate in the gas phase shows seven intense peaks. Out of the seven peaks in the neutral trans conformer, the first and last peaks in the trans conformer show bathochromic shifts of 0.5 and 0.9 nm, respectively, than in

the neutral gauche conformer, whereas the remaining peaks show hypsochromic shifts of 2.3, 4.5, 0.3, 3.2, and 1.5 nm. Neutral gauche ethyl formate exhibits very strong light absorption near 86.4 nm ($\varepsilon = 38\,213$) and weak absorption at 131 nm ($\varepsilon = 6597$), whereas the neutral trans conformer exhibits very strong light absorption at 86.7 nm ($\varepsilon = 35\,378$) and weak absorption at 130.1 nm ($\varepsilon = 7615$).

Comparative electronic absorption spectra of trans and cis conformers of methyl formate in the gas phase and in astrophysical H$_2$O ice are shown in Figure 11. The absorption spectra of trans and cis conformers of methyl formate in the gas phase show eight intense peaks each. Of these eight peaks, the first two peaks show 0.1 and 2 nm bathochrmic shifts and the remaining six peaks show hypsochromic shifts of 1.6, 1.6, 6.5, 9.4, 10.7, and 1.2 nm, respectively. The neutral trans conformer of methyl formate exhibits very strong light near 84.3 nm ($\varepsilon = 37\,685$) and weak absorption at 131.2 nm ($\varepsilon = 10\,892$), whereas the neutral cis conformer shows strong absorption at 51 nm ($\varepsilon = 41\,685$) and weak absorption at 130 nm ($\varepsilon = 6922$).

4. ASTROPHYSICAL IMPLICATIONS

Though some modes are common to both trans and gauche conformers of ethyl formate, it is possible to differentiate their vibrational spectra. We suggest lines especially good for observing trans and gauche conformers and their ions from an astrophysical point of view. There are four common lines for neutral trans and gauche conformers. These are at 8.5, 5.9, 3.35, and 3.39 μm. For the last two lines at 3.35 and 3.39 μm the IR intensity for both eutral conformers is almost the same. These lines correspond to the C−H stretch and CH$_2$ symmetric stretching mode, respectively. However, using the remaining two common lines, we can differentiate the neutral trans and gauche conformers. These lines are at 8.5 and 5.9 μm, corresponding to the C−O stretch and C=O stretch, respectively. If the line at 8.5 μm is more intense than at 5.9 μm, then the conformer is the trans conformer. When the opposite is true, the conformer is the gauche conformer. Apart from these, one more additional line at 8.8 μm corresponding to the CH$_2$ rock is about 42 times more intense in the gauche conformer of the neutral ethyl formate than the neutral trans conformer. From these three lines we can differentiate the neutral trans and gauche conformers.

For the cation of the trans conformer as well as the gauche conformers, the line at 6.4 μm is the most intense line, which corresponds to the C=O stretch. For the former this line is more intense than the latter. The cation of the trans and gauche conformers can be differentiated by the line at 7.64 μm and corresponds to the H in plane vibration with O−C=O plane. This is the second most intense line for the cation of the gauche conformer, which is absent for the cation of the trans conformer. The common lines for the anion of the trans and gauche conformers are at 3.78, 7.18, 9.1, and 3.37 μm, corresponding to the C−H stretch, C=O stretch, C−O stretch, and CH$_3$ asymmetric stretch, respectively. The IR intensity of the most intense line at 3.78 μm is about twice that of the second intense line at 7.18 μm for the trans conformer, whereas it is three times more intense than that of the second most intense line for the gauche conformer. The CH$_2$ symmetric stretching line at 2.49 μm is two times more intense for the gauche conformer than that of trans conformer.

It is easy to identify the trans or cis conformer of methyl formate from the observed spectra. Almost all peaks of the neutral trans and cis conformers of methyl formate in the gas phase differ by 0.05 μm except the H out of plane to the OCO plane, the CH_2 rock, and the CH_3 asymmetric stretch. These modes are observed at the same frequency and of the same IR intensity. Recently Kobayashi et al.[44] reported the cis conformer of torsionally excited methyl formate in the Orion KL. From our study the cis conformer of methyl formate in neutral, its ions in gas, and the neutral in H_2O ice phase show significant changes in the infrared as well as electronic absorption spectra. The most intense peak in the neutral cis conformer in the gas phase is the C=O stretch, which is observed at 5.878 μm, whereas this mode in H_2O ice is observed at 6.242 μm. The torsionally excited mode shows a significant difference in the wavelength. A largest difference of 1.8 μm is observed for the C—O stretching mode in the gas phase and in H_2O ice.

5. CONCLUSION

We studied vibrational and electronic absorption spectra of trans and gauche conformers of the neutral, cation, and anion of ethyl formate and trans and cis conformers of methyl formate in gas and neutral conformers in astrophysical H_2O ice at the MP2/TZVP level of theory. The trans conformer of ethyl formate is more stable than its gauche conformer, whereas the cis conformer of methyl formate is more stable than its trans conformer. The vibrational frequencies from this work for both conformers of neutral ethyl formate are in agreement with experimental determinations. The neutral cis conformer of methyl formate shows a significant change in its infrared and electronic absorption spectra when studied in astrophysical H_2O ice. All transitions in trans and gauche conformers of neutral ethyl formate as well as their ions are $\sigma \rightarrow \sigma^*$ transitions. Lines especially good for observing experimentally for the neutral, cation, and anion of both conformers are suggested. The neutral trans and gauche conformers can be differentiated by the IR intensities of three common lines at 8.5, 5.9, and 8.8 μm, which correspond to the C—O stretch, C=O stretch, and CH_2 rock vibrations, respectively. The neutral cis conformer of methyl formate in the gas phase and in H_2O ice can be differentiated by the lines for the C=O stretch, CO stretch, CH_3 symmetric deformation, and OCO stretch. These modes differ by 0.36, 1.8, 0.35, and 0.64 μm, respectively, in the gas phase and in H_2O ice. The first three modes are red-shifted and a remaining mode is blue-shifted in the neutral cis conformer of methyl formate in the gas phase than in H_2O ice.

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■ REFERENCES

(1) Spitzer, L. *Physical Processes in the Interstellar Medium*; John Wiley & Sons: New York, 1978

(2) Papoular, R.; Conard, J.; Guillois, O.; Nenner, I.; Reynaud, C.; Rouzaud, J. N. *Astron. Astrophys.* **1996**, *315*, 222–236.

(3) Henning, T. H.; Salama, F. *Science* **1998**, *282*, 2204–2210.

(4) Omont, A. *J. Chem. Soc., Faraday. Trans.* **1993**, *89*, 2137–2145.

(5) Bujarrabal, V.; Fuente, A.; Omont., A. *Astron. Astrophys.* **1994**, *285*, 247–271.

(6) Mathis, J. S.; Metzger, P. G.; Panagia, N. *Astron. Astrophys.* **1983**, *128*, 212–229.

(7) Irvine, W. M.; Goldsmith, P. F.; Hajlmarson, A. A. In *Interstellar Processes*; Hollenbach, D. J., Thronson, H. A., Eds.; Reidel: Dordrecht, The Netherlands, 1987; pp 561−610.

(8) Ohishi, M.; Kaifu, N. *Faraday Discuss.* **1998**, *109*, 205–216.

(9) Winnewisser, G.; Kramer, C. *Space. Sci. Rev.* **1999**, *90*, 181–202.

(10) Omont, A. *Rep. Prog. Phys.* **2007**, *70*, 1099–1176.

(11) Ehrenfreund, P.; Charnley, S. B. *Annu. Rev. Astron. Astrophys.* **2000**, *38*, 427–483.

(12) Müller, H. S. P.; Schlöder, F.; Stutzki, J.; Winnewisser, G. *J. Mol. Struct.* **2005**, *742*, 215–227.

(13) Whittet, D. C. B.; Walker, H. *J. Mon. Not. Roy. Astro. Soc.* **1991**, *252*, 63–67; and references therein.

(14) Hollis, J. M.; Remijan, A. J.; Jewell, P. R.; Lovas, F. J. *Astrophys. J.* **2006**, *642*, 933–939; and references therein.

(15) McGonagle, D.; Irvine, W. M.; Minh, Y. C.; Ziurys, L. M. *Astrophys. J.* **1990**, *359* (1), 121–124; and references therein.

(16) Bottinelli, S.; Ceccarelli, C.; Le floch, B.; Williams, J. P.; Castets, A.; Caux, E.; Cazaux., S.; Maret, S.; Parise, B.; Tielens, A. G. G. M. *Astrophys. J.* **2004**, *615*, 354–358; and references therein.

(17) Pathak, A.; Rastogi, S. *Chem. Phys.* **2006**, *326*, 315–328; and references therein.

(18) Mattioda, A. L.; Hudgins, D. M.; Allamandola, L. J. *Astrophys. J.* **2005**, *629*, 1188–1210; and references therein.

(19) Hollis, J. M.; Lovas, F. J.; Remijan, A. J.; Jewell, P. R.; Ilyushin, V. V.; Kleiner, I. *Astrophys. J. Lett* **2006**, *643*, L25–L28; and references therein.

(20) Snyder, L. E.; Lovas, F. J.; Hollis, J. M.; Friedel, D. N.; Jewelle, P. R.; Remijan, A.; Ilyushin, V. V.; Alekseev, E. A.; Dyubko, S. F. *Astrophys. J.* **2005**, *619* (2), 914–930.

(21) Miao, Y.; Mehringer, D. M.; Kuan, Y.-J.; Snyder, L. E. *Astrophys. J. Lett.* **1995**, *445*, L59–L62.

(22) Schilke, P.; Benford, D. J.; Hunter, T. R.; Lis, D. C.; Phillips, T. G. *Astrophys. J.* **2001**, *132* (Suppl.), 281–364.

(23) Schilke, P.; Groesbeck, T.; Blake, G.; Phillips, T. G. *Astrophys. J.* **1997**, *108* (Suppl.), 301–337.

(24) Cazaux, S.; Tielens, A. G. G. M.; Ceccarelli, C.; Castets, A.; Wakelam, V.; Caux, E.; Parise, B.; Teyssier, D. *Astrophys. J. Lett.* **2003**, *593*, L51–L55.

(25) Charnley, S. B.; Kress, M. E.; Tielens, A. G. G. M.; Miller, T. J. *Astrophys. J.* **1995**, *448*, 232–239.

(26) Riveros, J. M.; Wilson, E. B., Jr. *J. Chem. Phys.* **1967**, *46*, 4605–4612.

(27) Karpovitch, J. *J. Chem. Phys.* **1954**, *22*, 1767–1773.

(28) Tabuchi, D. *J. Chem. Phys.* **1958**, *28*, 1014–1021.

(29) Peng, Z.; Shylkov, S.; Van Alsenoy, C.; Geise, H. J.; Van der Veken, B. *J. Phys. Chem.* **1995**, *99*, 10201–10212.

(30) Meyer, R.; Wilson, E. B., Jr. *J. Chem. Phys.* **1967**, *53*, 3969–3980.

(31) Kaushik, V. K. *Chem. Phys. Lett.* **1980**, *70*, 317–320.

(32) Medvedev, I. R.; De Lucia, F. C.; Herbst, E. *Astrophys. J., Suppl. Ser.* **2009**, *181*, 433–438.

(33) Demaison, J.; Boucher, D.; Burie, J.; Dubrulle, A. *Z. Naturforsch.* **1984**, *39a*, 560–564.

(34) Charles, S. W.; Jones, G. I. L.; Owen, N. L.; Cyvin., S. J.; Cyvin, B. N. *J. Mol. Struct.* **1973**, *16*, 225–257.

(35) Maes, I. I.; Herrebout, W. A.; Van der Veken, B. J. *J. Raman Spectrosc.* **1994**, *25*, 679–691.

4755

dx.doi.org/10.1021/jp112373k |*J. Phys. Chem. A* 2011, 115, 4743–4756

(36) Belloche, A.; Garrod, R. T.; Muller, H. S. P.; Menten, K. M.; Comito, C.; Schilke, P. *Astron. Astrophys.* **2009**, *499*, 215–232.

(37) Brown, R. D.; Crofts, J. G.; Godfrey, P. D.; Gardner, F. F.; Robinson, B. J.; Whiteoak, J. B. *Astrophys. J.* **1975**, *197*, L29–L31.

(38) Bauder, A. *J. Phys. Chem. Ref. Data* **1979**, *8*, 583–618.

(39) Plummer, G. M.; Herbst, E.; De Lucia, F. C.; Blake, G. A. *Astrophys. J.* **1984**, *55* (Suppl), 633–656.

(40) Plummer, G. M.; Herbst, E.; De Lucia, F. C.; Blake, G. A. *Astrophys. J.* **1986**, *60* (Suppl.), 949–961.

(41) Chao, J.; Hall, K. R.; Marsh, K. N.; Wilhoit, R. C. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1369–1436.

(42) Plummer, G. M.; Herbst, E.; De Lucia, F. C. *Astrophys. J.* **1987**, *318*, 873–875.

(43) Odashima, H.; Ogata, K.; Takagi, K.; Tsunekawa, S. *J. Mol. Spectrosc.* **2001**, *210*, 196–212.

(44) Kobayashi, K.; Ogata, K.; Tsunekawa, S.; Takano, S. *Astrophys. J.* **2007**, *657*, L17–L19.

(45) Oesterling, L. C.; Albert, S.; De Lucia, F. C. *Astrophys. J.* **1999**, *521*, 255–260.

(46) Senent, M. L.; Villa, M.; Meléndez, F. J.; Gómez, R. D. *Astrophys. J.* **2005**, *627*, 567–576.

(47) Carvajal, M.; Willaert, F.; Demaison, J.; Kleiner, I. *J. Mol. Spectrosc.* **2007**, *246*, 158–166.

(48) Margules, L.; Coudert, L. H.; Mollendal, H.; Guillemin, J. −C.; Huet, T. R.; Janečkova, R. *J. Mol. Spectrosc.* **2009**, *254*, 55–68.

(49) Ilyushin, V.; Kryvda, A.; Alekseev, E. *J. Mol. Spectrosc.* **2009**, *255*, 32–38.

(50) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503–506.

(51) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275–280.

(52) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281–289.

(53) Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, *220*, 122–128.

(54) Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989**, *154*, 83–89.

(55) Cancés, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041.

(56) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158.

(57) Tomasi, J.; Mennucci, B.; Cancés, E. *J. Mole. Structure (THOECHEM)* **1999**, *464*, 211–226.

(58) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch., M. J. *J. Phys. Chem.* **1996**, *100*, 16098–16104.

(59) Gorelsky, S. I. SWizard program, http://www.sg-chem.net/, University of Ottawa, Ottawa, Canada, 2009.

(60) *NIST Computational Chemistry Comparison and Benchmark Database*, NIST Standard Reference Database Number 101, 2010, http://cccbdb.nist.gov.

(61) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Omasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li. X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian: Wallingford, CT, 2004.

(62) Blom, C. E.; Günthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267–271.