Published in final edited form as:
ACS Earth Space Chem. 2019 ; 3(7): 1182–1188. doi:10.1021/acsearthspacechem.9b00058.

Solid-State Isomerization and Infrared Band Strengths of Two Conformational Isomers of Cyclopropanecarboxaldehyde, A Candidate Interstellar Molecule

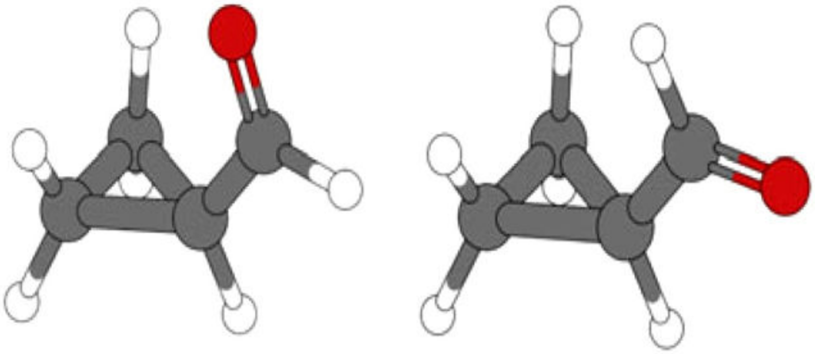
Reggie L. Hudson[1,*], **Falvia M. Coleman**[1]

[1]Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

Abstract

At least a dozen of the known interstellar molecules possess a formyl group (HCO), suggesting that other such species exist and await discovery in the interstellar medium. Here we examine the mid-infrared (mid-IR) spectrum and selected physical properties of one such candidate, cyclopropanecarboxaldehyde, in amorphous ices. Mid-IR transmission spectra of solid cyclopropanecarboxaldehyde are presented for the first time and used to determine the *cis*-to-*trans* ratio of conformational isomers present in amorphous samples. The measured ratio is compared to one from an electron-diffraction study of the gas-phase compound. The *cis*-to-*trans* isomerization in the amorphous compound is followed and the activation energy is determined. The first IR band strengths for solid cyclopropanecarboxaldehyde are reported. Also presented are refractive indices and densities at 15 K for amorphous forms of two related compounds, cyclopropane and cyclopropanemethanol. Two low-temperature reactions for the interstellar formation of cyclopropanecarboxaldehyde are briefly described.

Graphical Abstract



Keywords

IR spectroscopy; band strengths; astrochemistry; amorphous solids; ices

---

[*]Corresponding author. reggie.hudson@nasa.gov (R. L. Hudson).

1. INTRODUCTION

Over 200 molecules and molecular ions have been reported to be present in the gas phase of the interstellar medium (ISM), and to these can be added about six firm spectroscopic identifications in interstellar ices, and about six other solid-phase identifications that are more tentative.[1,2] With all of these in hand it is possible to search for trends and to identify molecular families from which to make predictions of as yet undiscovered species. In this paper, we consider one such molecular family and use it as motivation for new solid-phase measurements on one of its members and two related compounds.

Figure 1 shows structures for twelve reported interstellar gas-phase molecules, the common structural unit for each being the formyl group, HCO. These molecules are taken from the review by McGuire, which should be consulted for the original citations.1 In the first row is the simplest of these molecules, formaldehyde (a), followed by three isoelectronic species, formic acid (b), formamide (c), and acetaldehyde (d), and others in the second and third rows of the figure. The astronomical origins of these interstellar molecules are uncertain, but multiple reports have shown that some of them can be made in laboratory ices. For example, ion-irradiation of H_2O + CO ices produces formic acid (b), while a similar UV-photolysis experiment with NH_3 + CO ices makes formamide (c).[3,4] From decades earlier are the studies of Milligan and Jacox on these same ice mixtures.[5,6] More-recent examples include ice experiments showing the synthesis of acetaldehyde (d) from electron irradiation of a CH_4 + CO ice mixture and of glycolaldehyde (k) from CH_3OH + CO.[7,8]

Given the many HCO-containing molecules in Figure 1 it seems safe to predict that others of this type are present in the interstellar medium. One such molecular type would consist of a formyl-containing molecule with a cyclic functional group, either an aliphatic or aromatic ring. While there is an extensive astrochemical literature on aromatic rings, far less information is available related to aliphatic rings. Figure 2 shows the smallest saturated carbon ring, the prototypical cyclopropane (a), alongside cyclopropanecarboxaldehyde (b), and cyclopropanemethanol (c). Although cyclopropane lacks a dipole moment and so cannot be detected with radio telescopes, such is not the case with (b) and (c). The aldehyde (b) is particularly attractive for study as it possesses the formyl group of the many interstellar molecules of Figure 1.

Aside from astrochemical considerations, cyclopropanecarboxaldehyde, (b) in Figure 2, has properties of intrinsic interest. Its gas-phase conformations were shown by Bartell and Guillory to differ from expectations drawn from acetaldehyde, with only two orientations for the former in contrast to the three-fold rotational barrier of the latter.[9] The two conformations of cyclopropanecarboxaldehyde, which we designate as the *cis* and *trans* forms, are shown in Figure 3, with the *cis* isomer being the one with its carbonyl group over the cyclopropyl ring. The gas-phase room-temperature *cis*-to-*trans* ratio of these isomers was found by electron diffraction to be about 55:45, again by Bartell and Guillory, but no solid-state comparison is available. This raises an important question about whether both isomers can exist in low-temperature amorphous ices, which are of considerable astrochemical interest.

Here we continue our studies of the IR spectra and properties of small molecules known or suspected to be extraterrestrial. We present new laboratory results on cyclopropanecarboxaldehyde in the solid state, including the first transmission IR spectra of cyclopropanecarboxaldehyde in an amorphous ice, direct evidence that two conformers are present, a direct measurement of the *cis*-to-*trans* ratio of these isomers, and data on the conversion of one isomer into the other. These new results were obtained by recording mid-IR transmission spectra of samples of known thickness and IR path length. A band strength is reported for one IR absorbance of the *cis* isomer and one for the *trans*, from which other band strengths can be determined as needed. Our results are compared to older electron diffraction and to computational studies. In addition, we also report the first measurements of several physical properties of amorphous solid forms of cyclopropanecarboxaldehyde and two related molecules.

These new results constitute data needed for future laboratory astrochemical investigations, such as the calculation of abundances of reaction products and measurements of ice composition. Just as important as our numerical results are conceptual ones. Specifically, the work presented here provides evidence that although complex organic molecules are trapped in interstellar ices, such molecules are not necessarily immobile. Conformational changes can be initiated in ices on warming, with implications for the isomeric form of a molecule present and what is subsequently released into the gas phase. The motion of hydrogen atoms, for example, at interstellar temperatures near 10 K is well known, but we are unaware of examples in the astrochemical literature of intramolecular motion involving reasonably complex molecules such as the aldehyde we have studied in this work. Conventional chemical experience suggests that such variations in molecular structure can have implications for reactivity and reaction products. Therefore, our results immediately suggest several new lines of investigation involving cyclopropanecarboxaldehyde's formation and destruction. See our Discussion section.

Before describing our results we recall Johnson's observation that "Every language has its anomalies, which ... must be tolerated".[10] In the present case, several names are associated with the molecule of Figure 3. The one used in this paper appears to be that most often met in the astrochemical literature, but one also finds cyclopropyl carboxaldehyde, cyclopropylcarboxaldehyde, cyclopropanecarbaldehyde, cyclopropane carboxaldehyde, and perhaps others. Also, the *cis* and *trans* isomers of our Figure 3 are sometimes referred to as *syn* and *anti* conformers, respectively.

2. EXPERIMENTAL

Only a summary of our methods is given here, as they have been described in recent papers from our group.[11,12,13]

All compounds were purchased from Sigma Aldrich and used as received other than routine degassing for cyclopropanemethanol and cyclopropanecarboxaldehyde. The latter compound was refrigerated (3 °C) when not in use. No differences in results were found between samples that were newly arrived from the supplier and those that had been used for several weeks.

Ice samples were prepared by condensing the room-temperature vapor for each compound onto a pre-cooled KBr substrate (10 - 16 K) inside a vacuum chamber ($\sim 10^{-8}$ torr) at a rate that increased the resulting ice's thickness by a few micrometers per hour. Sample thicknesses ranged from about 0.5 to 3 μm, a variation that was not found to influence any of the final results except for the observed peak heights and band areas, as expected.

Infrared spectra were recorded with a Thermo iS50 spectrometer at a resolution of 1 cm^{-1} from 5000 to 500 cm^{-1}, usually with 200 accumulations (scans) per spectrum. The exception was when relatively rapid spectral changes were studied at 83 K (*vide infra*), in which case only 10 scans were used. A few measurements were made with higher resolutions (e.g., 0.5 cm^{-1}), but the widths of the IR bands were such that little or no additional information was obtained. In all cases, the IR beam of the spectrometer was aligned perpendicular to the plane of the sample.

The thickness of each ice was determined by measuring interference fringes, using a 670-nm laser, during the sample's deposition.[14] This approach required a knowledge of the sample's refractive index (n_{670}), which we measured by two-laser interferometry.[15] Both the high vacuum ($\sim 10^{-8}$ torr) and ultra-high vacuum (UHV, $\sim 10^{-10}$ torr) systems employed in our recent work were used to measure refractive indices, but in practice the use of UHV conditions was hardly worth the extra cost and effort involved since the two vacuum systems gave results within experimental error. However, our UHV set-up also was equipped with a quartz crystal microbalance with which we measured the density (ρ) of each compound, a quantity needed to compute IR band strengths. Therefore, all the values of n_{670} and ρ used in this paper refer to measurements under UHV conditions. See the work of Satorre and colleagues for similar measurements on other molecules.[16]

3. RESULTS

Our focus in this paper is on cyclopropanecarboxaldehyde, but data for the three molecules in Figure 2 are so scarce that Table 1 gives the refractive indices (n_{670}) and mass densities (ρ) we measured at 15 K for amorphous forms of all three compounds, each value being the average of at least three determinations. A number density (ρ_N) for each compound also is listed, calculated from $\rho_N = \rho\,(N_A / M)$ where N_A is Avogadro's constant and M is the molar mass of the compound in g mol^{-1}. The table's last two rows give specific (r) and molar (R_M) refractions, calculated from equations (1) and (2).

$$r = \left(\frac{1}{\rho}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{1}$$

$$R_M = \left(\frac{M}{\rho}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{2}$$

The trend in our R_M values (hydrocarbon < aldehyde < alcohol) matches what can be calculated from liquid-phase data and equation (2), but the extent to which R_M for these three molecules is influenced by optical exaltation is unknown.

Figure 4 shows a mid-IR transmission spectrum of cyclopropanecarboxaldehyde deposited at 13 K from the room-temperature vapor, apparently the first publication of a transmission IR spectrum of a solid form of this compound. This spectrum resembles that of Durig and Little, with the qualification that their spectrum was obtained in a reflection mode with the sample deposited on a "blackened brass plate" near 77 K.[17] The same research group published band assignments and an extensive vibrational analysis in that paper and subsequent ones[18,19,20], to which the reader is directed for details.

The stronger features in the spectrum of Figure 4 fall into three regions, the CH and CH_2 group vibrations at 3100 - 2800 cm^{-1}, the intense carbonyl feature near 1700 cm^{-1}, and the fingerprint region at 1500 - 500 cm^{-1}. An enlargement of the latter is shown in Figure 5, where the rounded appearance of many of the IR bands in the bottom trace suggests that the ice sample was an amorphous solid.[21] This was confirmed by a significant and irreversible sharpening of many IR features on warming to ~110 K and higher, the result being shown in the uppermost trace of Figure 5 in a spectrum we assign to crystalline cyclopropanecarboxaldehyde. Further warming to 150 K resulted in complete sublimation of the sample over several minutes.

An enlargement of the 1000 - 900 cm^{-1} region of cyclopropanecarboxaldehyde's IR spectrum is shown in Figure 6, and is the key region for the remainder of this paper. The two large peaks in the bottom spectrum are assigned to the compound's *cis* (959 cm^{-1}) and *trans* (925 cm^{-1}) conformers, again following Durig and co-workers.[17] More specifically, the two IR bands are due to a combination of ring deformation and stretching motions of the C-C bond between the ring and the formyl group. Computations at multiple levels of theory fully support these assignments.[22]

On warming the sample of Figure 6 from 13 to 85 K, we observed a slow decrease in intensity for the *cis* peak at 959 cm^{-1} and a concomitant rise in the *trans* peak at 925 cm^{-1}, corresponding to a *cis* → *trans* conformational change. This is better seen in Figure 7, which also shows that no variations in bandwidth were apparent during this transformation. An isosbestic point is seen near 942 cm^{-1}. After crystallization, only the *trans* form was observed.

From spectra like those of Figures 5 - 7, we calculated both the fractions of *cis* and *trans* isomers in our ices as well as IR band strengths. The column density of just the *cis* conformer is related to the area of the IR band at 959 cm^{-1} and to that band's intrinsic strength, which we denote as A', in cm $molecule^{-1}$, according to

$$N_{cis} = \frac{2.303 \int^{band} (Absorbance_{cis})\, d\tilde{\nu}}{A'_{cis}} \tag{3}$$

with a similar relation applying to the *trans* conformer. – The factor of 2.303 = ln(10) is needed to convert from the base-10 absorbance scale to an optical depth scale in base e. – Knowing that the total column density N is the sum of column densities of *cis* and *trans* conformers gives

$$N = \frac{2.303\int^{band}(Absorbance_{\ cis})d\tilde{v}}{A'_{cis}} + \frac{2.303\int^{band}(Absorbance_{\ trans})d\tilde{v}}{A'_{trans}} \tag{4}$$

and rearrangement leads to

$$\int^{band}(Absorbance_{\ cis})\,d\tilde{v} = \left(\frac{-A'_{cis}}{A'_{trans}}\right)\int^{band}(Absorbance_{\ trans})\,d\tilde{v} + \frac{NA'_{cis}}{2.303} \tag{5}$$

which is the equation of a straight line with slope ($-A'_{\text{cis}}$ / A'_{trans}) and intercept ($N\,A'_{\text{cis}}$/ 2.303). From runs such as the one in Figure 7, we measured band areas and plotted them as in Figure 8. The resulting slope and intercept gave $A'_{\text{cis}} = 1.69 \times 10^{-17}$ and $A'_{\text{trans}} = 1.21 \times 10^{-17}$ cm molecule^{-1} for a ratio (A'_{cis} / A'_{trans}) = 1.40, with the ice's column density (N, molec cm^{-2}) in this last equation being known from measurements of the sample's thickness and density.

For Figure 7, the fraction of the *cis* isomer in the ice at each stage of the isomerization is

$$f_{\ cis} = \frac{\int^{band}(Absorbance_{\ cis})\,d\tilde{v}}{\int^{band}(Absorbance_{\ cis})\,d\tilde{v} \ + \ (ratio)\int^{band}(Absorbance_{\ trans})\,d\tilde{v}} \tag{6}$$

where "ratio" ≈ 1.40 is found from the line in Figure 8. Table 2 gives the resulting *cis* and *trans* fractions for the data of Figures 7 and 8. We emphasize that these numbers are not equilibrium fractional abundances, but rather mole fractions during a reaction, showing the smooth conversion of one conformer into the other. Lowering the temperature after the reaction was underway never restored the starting fractions of *cis* and *trans* isomers.

In a different type of experiment, by holding an amorphous ice at a single temperature and recording its spectrum over time, we were able to gather kinetic data, the *cis* → *trans* change following first-order kinetics. Rate constants were extracted in the usual manner and the Arrhenius plot of Figure 9 was produced from them. – The useful range for such measurements was 65 - 83 K, as below 65 K the reaction was too slow to reliably measure the *cis* → *trans* conversion and above 83 K it was too fast. Holding an ice at 60 K for several days failed to produce detectable spectral changes. – The slope of the line in Figure 9 gave an activation energy (E_{act}) of 18 kJ mol^{-1} = 1500 cm^{-1} for the *cis* → *trans* change of cyclopropanecarboxaldehyde, the conversion factor being 1 kJ mol^{-1} = 83.7 cm^{-1}. The uncertainty in our E_{act} is estimated to be on the order of 1 kJ mol^{-1}.

Returning to Figure 5, close inspection shows that not only is the *cis* → *trans* conversion accompanied by changes in the 959/925 cm^{-1} region, but changes also are seen at 1362/1318 cm^{-1} and 674/509 cm^{-1}. However, neither of these regions was used for our analyses, in the first case because of a sloping baseline near the 1362 cm^{-1} peak that produced an uncertainty in the integration limits, and in the second because of the 674/509 cm^{-1} pair's weakness.

A few experiments were carried out in which cyclopropylcarboxaldehyde was mixed with another ice to assess the influence of the ice matrix. As expected, the peaks in our IR spectra could be sharpened by using matrix-isolation techniques, specifically with an N_2 + cyclopropanecarboxaldehyde ice (~100:1). However, the desirability and aesthetic appeal of sharp peaks was offset by the need to accurately know the column density (N) of molecules in our samples, which was more accurately found with single-component ices. Although the two peaks of interest, near 960 and 929 cm^{-1} in this N_2-rich sample, were clearly seen, as the ice was warmed from its initial 14 K, the N_2 matrix began subliming at 25 - 30 K, so that by 35 K the spectrum resembled that of pure cyclopropanecarboxaldehyde, and so no new information was obtained on the *cis*-*trans* conversion.

In a final experiment, we recorded the spectrum of cyclopropanecarboxaldehyde trapped in amorphous H_2O-ice at 15 K (~10:1). The spectral features of the amorphous H_2O-ice were scarcely altered, aside from a small sharpening near 1690 cm^{-1} in the bending mode, overlapping with the aldehyde's carbonyl peak. Only the stronger cyclopropanecarboxaldehye bands were visible, and only where there was little or no overlap with the IR bands of H_2O-ice, such as the aldehyde feature at 1362 cm^{-1}, which was shifted to 1366 cm^{-1} in the H_2O-rich mixture. Most importantly, the aldehyde's two bands in the 980 - 900 cm^{-1} region were clearly seen, at 967 and 929 cm^{-1}. Warming brought about the expected decrease in the *cis* feature, but overlap with, and shifts in, the broad H_2O-ice libration band near 800 cm^{-1} made measurements of the growth of the *trans* isomer's peak near 929 cm^{-1} difficult. Nevertheless, although quantitative measurements were impossible, there was no doubt that both aldehyde conformers were present in H_2O-ice and that their relative abundances were temperature dependent. The aldehyde was retained in the H_2O-ice until the latter's sublimation. Additional work on such mixtures is planned.

4. DISCUSSION

Our *cis*-to-*trans* ratio of cyclopropanecarboxaldehyde conformers trapped from the gas phase is 50:50, close to the 55:45 ratio reported by Bartell and Guillory9, suggesting that the room-temperature distribution of gas-phase isomers was maintained when the cyclopropanecarboxaldehyde vapor condensed into an amorphous solid near 13 K. This appears to be the first such direct comparison between the gas and amorphous-solid phases of this compound. Our results also show that although the *trans* form is the only isomer present in the polycrystalline solid[17], such is not the case for amorphous ices.

The ratio of our IR band strengths, $A'_{\mathrm{cis}}(959\ \mathrm{cm}^{-1}) / A'_{\mathrm{trans}}(925\ \mathrm{cm}^{-1})$, is ~1.4 reasonably close to the gas-phase value of ~1.6 calculated by Trindle and co-workers.[22] Certainly the order $A'_{\mathrm{cis}} > A'_{\mathrm{trans}}$ for the solid phase can be considered as confirmed experimentally. Density functional calculations with explicit considerations of the medium's polarity might improve the agreement.

The activation energy we found, 18 kJ mol^{-1} = 1500 cm^{-1}, for the *cis* → *trans* conformational change also appears reasonable when compared to calculated values, particularly given that the calculations were for the gas phase. See Table 9 of Trindle et al. for a summary, with calculated barriers ranging from about 1800 to 2500 cm^{-1}.[22]22 Our value also is close to the 18.4 kJ mol^{-1} = 1540 cm^{-1} of Volltrauer and Schwexdeman based on microwave measurements.[23]

Unfortunately, a detailed quantitative comparison of our work on *cis* and *trans* abundances to previous IR solid-phase results is impossible as earlier papers did not give sample thicknesses, a vertical scale with numbers, or spectra measured in a transmission mode. Moreover, the temperatures at which the published spectra of cyclopropanecarboxaldehyde solids were recorded were not stated, and the angle for reflection measurements was not provided. However, the agreement in terms of peak positions is excellent. Again, interested readers are referred to earlier papers for a full set of peak positions and assignments.[17,18,19,20]

We do not know the extent to which the method we have described for determining a *cis*-to-*trans* conformational ratio is applicable to other cyclopropyl systems. Our choice of cyclopropanecarboxaldehyde for study was prompted, in part, by the expected ~50:50 abundance ratio of conformers reported by Bartell and Guillory.9 It could be that our method is insufficiently sensitive for accurate results if one isomer is strongly dominating in abundance. Our method also requires unambiguous assignments of specific IR features to each isomer and a clean separation of the relevant IR bands. Clearly, additional work is needed on other molecules to determine the generality of the approach described here.

The formation of many interstellar organic molecules, and even some inorganics as small as H_2O, is thought to occur in ices and on grains in dense molecular clouds. Laboratory work has shown that dark-cloud conditions of low-temperature and ionizing radiation suffice to produce a large variety of chemical species. However, for the specific case of the molecule we have studied, cyclopropanecarboxaldehyde, there is a bias among terrestrial chemists that holds that 3-membered rings are relatively unstable, a bias not shared by the interstellar medium, where both ethylene oxide and propylene oxide have been identified by radio astronomers and low-temperature syntheses have been investigated.[24,25,26,27]

Low-temperature formation of cyclopropanecarboxaldehyde is likely to follow from two different directions, one from smaller molecules and one from a larger one. Cosmic radiation acting on frozen methane can produce both methylene (CH_2) and ethylene (C_2H_4), which combine to make cyclopropane. A C-H bond dissociation of the latter will give two radicals that are easily trapped by CO, a common interstellar-ice component, to make cyclopropanecarboxaldehyde. The final reaction is represented by (a) in Figure 10, which is reminiscent of the radiolytic formation of acetaldehyde from CO + CH_4 mentioned in our Introduction.

An alternative path to interstellar cyclopropanecarboxaldehyde comes from a large body of experimental work showing the oxidation of alcohols by radiation to give aldehydes and ketones. See, among many other examples, our recent study, and references therein, of the proton bombardment of ethanol and larger alcohols.[13] The suggested interstellar pathway is shown in (b) of Figure 10, solid cyclopropanemethanol being radiolytically oxidized to give the cyclic aldehyde, with cyclopropanemethanol itself being made in an icy mixture of cyclopropane and methanol. That both CO and methanol are relatively abundant components of interstellar ices adds to the attraction of the reactions in Figure 10.

These considerations suggest several lines of astrochemical research. A solid-phase detection of cyclopropanecarboxaldehyde by IR methods seems unlikely given the extent of overlap of the aldehyde's strongest IR bands with those of other molecules, particularly H_2O, but a gas-phase observation might be possible. We note that rotational spectra are available for both the *cis* and *trans* isomers of cyclopropanecarboxaldehyde.[23] We also note that isomeric pairs involving two cyclic interstellar molecules have been identified, ethylene oxide and acetaldehyde and also propylene oxide and propanal. By extension, the detection[28] of propylene ($H_2C{=}CHCH_3$) suggests that cyclopropane, its radio-invisible cyclic isomer, is also interstellar. Similar arguments could be applied to the other two three-membered rings we studied (Figure 2) and their acyclic isomers.

For the laboratory astrochemist, our results have multiple uses. Direct applications of our data come from the band strengths, densities, and refractive indices in our Table I. For example, one can use our A' values and IR spectra to estimate yields in reactions where cyclopropanecarboxaldehyde is formed. In cases where ices containing the aldehyde are to be studied, it is important to have initial abundances or column densities or ice thicknesses, and our refractive indices (n) can be used to determine these quantities. In mixtures with the aldehyde, such as those that are H_2O rich, our n values will be useful in determining starting compositions. Finally, branching ratios for solid cyclopropanecarboxaldehyde destruction can be readily quantified using these same physical properties.

V. SUMMARY

Mid-IR transmission spectra of amorphous cyclopropanecarboxaldehyde have been presented for the first time. This new data shows that the *cis*-to-*trans* abundance ratio of about 1:1 in the gas-phase is maintained when cyclopropanecarboxaldehyde vapor is deposited to form an amorphous solid. The conversion of the *cis* conformer into the *trans* structure has been followed and an activation energy measured. An IR band strength for each conformer also has been measured, and the ratio of those band strengths compares favorably to results calculated by others. Density and index of refraction values for amorphous cyclopropane, cyclopropanecarboxaldehyde, and cyclopropanemethanol at 15 K are reported for the first time. The greater stability of the *trans* isomer over the *cis* was confirmed in two warmed amorphous ices.

ACKNOWLEDGEMENTS

Support from the NASA Astrobiology Institute through funding awarded to the Goddard Center for Astrobiology under proposal 13-13NAI7-0032 is acknowledged. Support also was received from NASA's Planetary Science Division Internal Scientist Funding Program through the Fundamental Laboratory Research (FLaRe) work package at the NASA Goddard Space Flight Center. The assistance of Ella Mullikin (Wellesley College), Robert Ferrante (U. S. Naval Academy), and Perry Gerakines (NASA Goddard Space Flight Center) in the early stages of this work is acknowledged. Our UHV chamber was constructed by Mark Loeffler (Northern Arizona University).

References

1. McGuire B 2018 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules. ApJS, 2018, 239, 1 – 48.
2. Boogert ACA; Gerakines PA; Whittet DCB Observations of the Icy Universe. Ann. Rev. Astron. and Astrophys, 2015, 53, 541 – 581.
3. Hudson RL; Moore MH Laboratory Studies of the Formation of Methanol and Other Organic Molecules by Water + Carbon Monoxide Radiolysis: Relevance to Comets, Icy Satellites, and Interstellar Ices. Icarus, 1999, 140, 451 – 461.
4. Demyk K; Dartois E; d'Hendecourt L; Jourdain de Muizon M; Heras AM; Breitfellner M Laboratory Identification of the 4.62 μm Solid State Absorption Band in the ISO-SWS Spectrum of RAFGL 7009S. Astron. & Astrophys, 1998, 339, 553 – 560.
5. Milligan DE; Jacox ME Infrared Spectrum and Structure of Intermediates in the Reaction of OH with CO. J. Chem. Phys, 1971, 54, 927 – 942.
6. Milligan DE; Jacox ME Matrix-Isolation Infrared Spectrum of the Free Radical NH_2. J. Chem. Phys, 1965, 43, 4487 – 4493.
7. Bennett CJ; Jamieson CS; Osamura Y; Kaiser RI A Combined Experimental and Computational Investigation on the Synthesis of Acetaldehyde [$CH_3CHO(X\ ^1A')$] in Interstellar Ices. Astrophys. J, 2005, 624, 1097 – 1115.
8. Hudson RL; Moore MH; Cook AM IR Characterization and Radiation Chemistry of Glycolaldehyde and Ethylene Glycol Ices. Adv. in Space Research, 2005, 36, 184 – 189.
9. Bartell LS; Guillory JP Electron-Diffraction Study of the Structure and Internal Rotation of Cyclopropyl Carboxaldehyde. J. Chem. Phys, 1967, 43, 647 – 653.
10. Johnson S Preface, A Dictionary of the English Language, 1755, London; W. Strahan.
11. Hudson RL; Loeffler MJ; Gerakines PA Infrared Spectra and Band Strengths of Amorphous and Crystalline N_2O. J. Chem. Phys, 2017, 146, 0243304.
12. Hudson RL; Gerakines PA Infrared Spectra and Interstellar Sulfur - New Laboratory Results for H_2S and Four Malodorous Thiol Ices. Astrophys. J, 2018, 867, 2 – 8.
13. Hudson RL; Moore MH Interstellar Ices and Radiation-Induced Oxidations of Alcohols. Astrophys. J, 2018, 857, 1 – 8.
14. Groner P; Stolkin I; Günthard HH Measurement of Deposition Rate in Matrix Spectroscopy with a Small Laser. J. Phys. E. - Sci. Instrum, 1973, 6, 122 – 123.
15. Tempelmeyer KE; Mills DW Refractive Index of Carbon Dioxide Cryodeposit. J. Appl. Phys, 1968, 39, 2968 – 2969.
16. Satorre MÁ; Domingo M; Millán C; Luna R; Vilaplana R; Santonja C Density of CH_4, N_2 and CO_2 Ices at Different Temperatures of Deposition. Planet. Space Sci, 2008, 56, 1748 – 1752.
17. Durig JR; Little TS Vibrational and Conformational Studies of Cyclopropanecarboxaldehyde. Croatica Chem. Acta, 1988, 61, 529 – 549.
18. Durig JR; Feng F; Little TS; Wang A-I Conformational Stability, Barriers to Internal Rotation, Structural Parameters, Ab lnitio Calculations, and Vibrational Assignment of Cyclopropanecarboxaldehyde. Structural. Chem, 1992, 3, 417 – 428.
19. Durig JR; Shen S Conformational Studies of Cyclopropane Carboxaldehydehyde from Temperature-Dependent FT-IR Spectra of Xenon Solutions. Spec. Acta, 2000, 56A, 2545 – 2561.
20. Durig JR; Yu Z; Shen S; Warren R; Verma VN; Guirgia GA Conformational Studies of Monosubstituted Three-Membered Rings by Variable Temperature FT-IR Spectra of Rare Gas Solutions. J. Molec. Struct, 2001, 563 - 564, 141 – 145.
21. Malherbe FE; Bernstein HJ Infrared Spectra of Rapidly Solidified Vapors. J. Chem. Phys, 1951, 19, 1607 – 1608.
22. Trindle C; Bleda EA; Altun Z Structure and Energetics of Cyclopropane Carboxaldehyde. Int. J. Quantum Chem, 2013, 113, 1155 – 1161.
23. Volltrauer HN; Schwendeman RH Microwave Spectra, Dipole Moments, and Torsional Potential Constants of cis- and trans-Cyclopropanecarboxyaldehyde. J. Chem. Phys, 1971, 54, 260 – 267.

24. Dickens JE; Irvine WM; Ohishi M; Ikeda M; Ishikawa S; Nummelin A; Hjalmarson A Hjalmarson Detection of Interstellar Ethylene Oxide (*c*-C_2H_4O). Astrophys. J, 1997, 489, 753 – 757. [PubMed: 11541726]

25. McGuire BA; Carroll PB; Loomis RA; Finneran IA; Jewell PR; Remijan AJ; Blake GA Discovery of the Interstellar Chiral Molecule Propylene Oxide (CH_3CHCH_2O). Science, 2016, 352, 1449 – 1552. [PubMed: 27303055]

26. Bennett CJ; Osamura Y; Lebar MD; Kaiser RI Laboratory Studies on the Formation of Three C_2H_4O Isomers - Acetaldehyde (CH_3CHO), Ethylene Oxide (*c*-C_2H_4O), and Vinyl Alcohol (CH_2CHOH) - in Interstellar and Cometary Ices. Astrophys. J, 2005, 634, 698 – 711.

27. Hudson RL; Loeffler MJ; Yocum KM Laboratory Investigations into the Spectra and Origin of Propylene Oxide, a Chiral Interstellar Molecule. Astrophys. J, 2017, 835, 225 – 233.

28. Marcelino N; Cernicharo J; Agúndez M; Roueff E; Gerin M; Martín-Pintado J; Mauersberger R; Thum C Discovery of Interstellar Propylene (CH_2CHCH_3): Missing Links in Interstellar Gas-Phase Chemistry. Astrophys. J 2007, 665, L127 – L130.

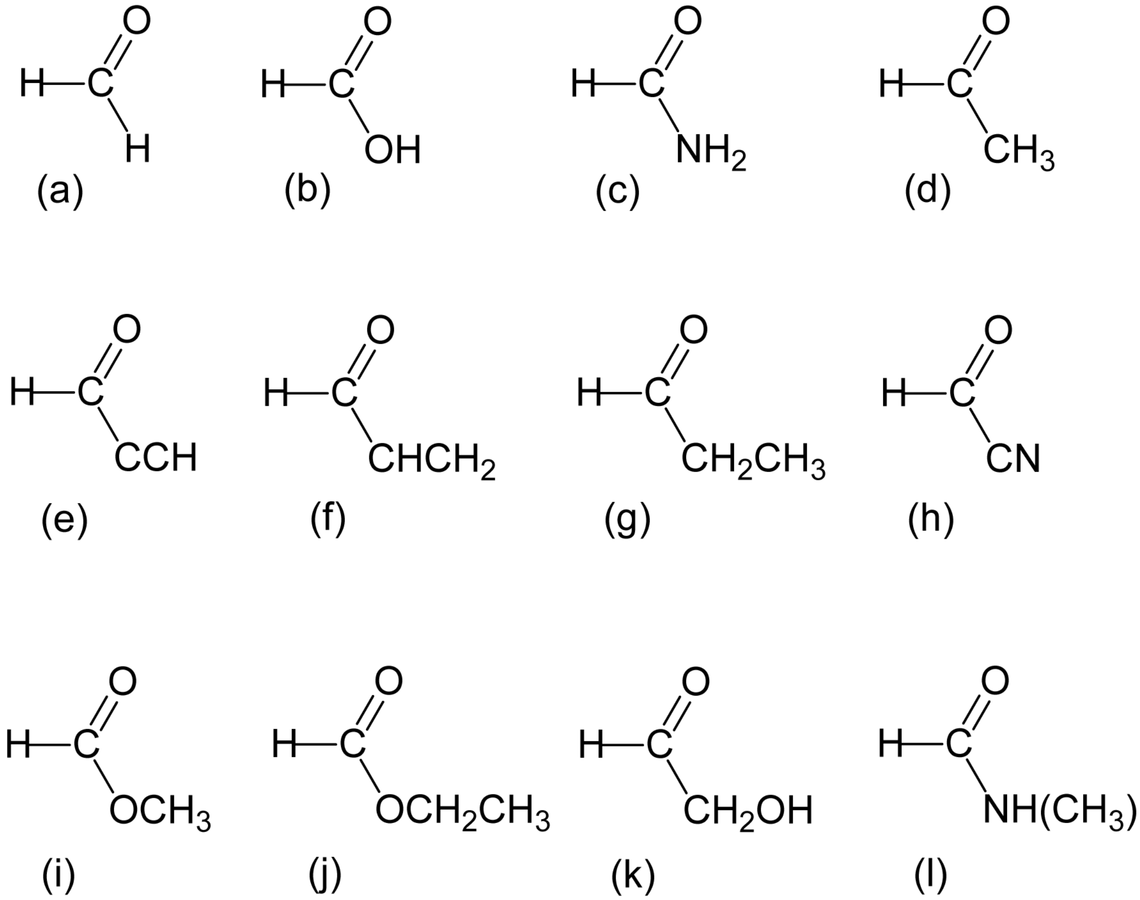


Figure 1.

Twelve gas-phase interstellar molecules possessing the formyl (HCO) group. The molecules are (a) formaldehyde, (b) formic acid, (c) formamide, (d) acetaldehyde, (e) propynal, (f) propenal, (g) propanal, (h) formyl cyanide, (i) methyl formate, (j) ethyl formate, (k) glycolaldehyde, and (l) methyl formamide. More than one name is used for some of these. See the review by McGuire for the citation to the astronomical discovery of each molecule.[1]

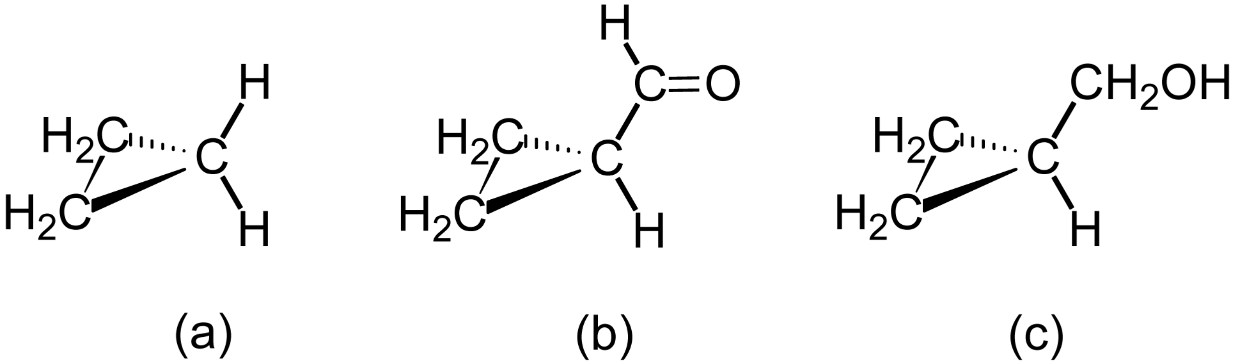


Figure 2.

Three molecules containing the cyclopropyl ring: (a) cyclopropane, (b) cyclopropanecarboxaldehyde, and (c) cyclopropanemethanol.

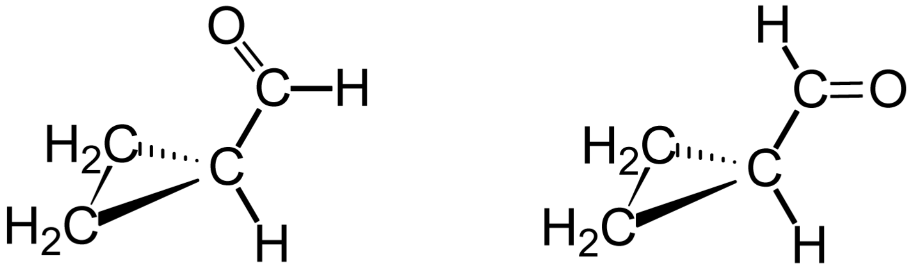


Figure 3.

The *cis* (left) conformation of cyclopropanecarboxaldehyde has the carbonyl (C=O) group above the cyclopropyl ring whereas the *trans* (right) conformation has it pointed away from the ring.

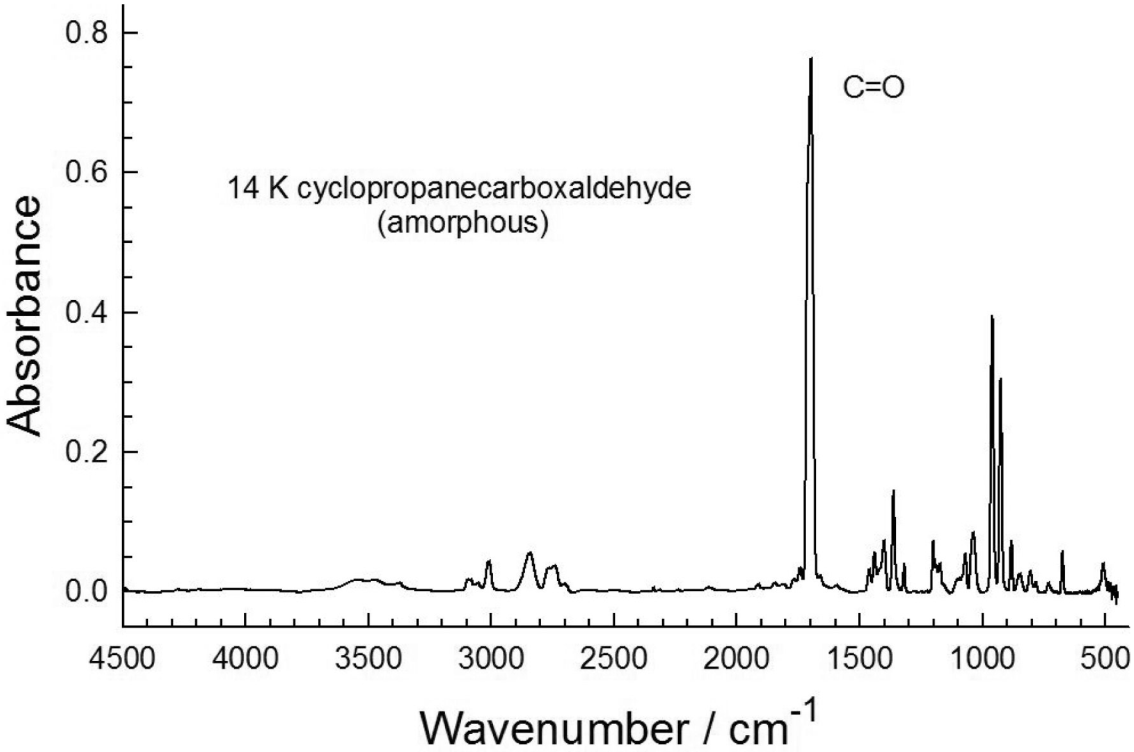


Figure 4.

Infrared survey spectra of cyclopropanecarboxaldehyde. The ice was made, and the spectrum recorded, at 13 K. The ice's thickness was about 2 μm.

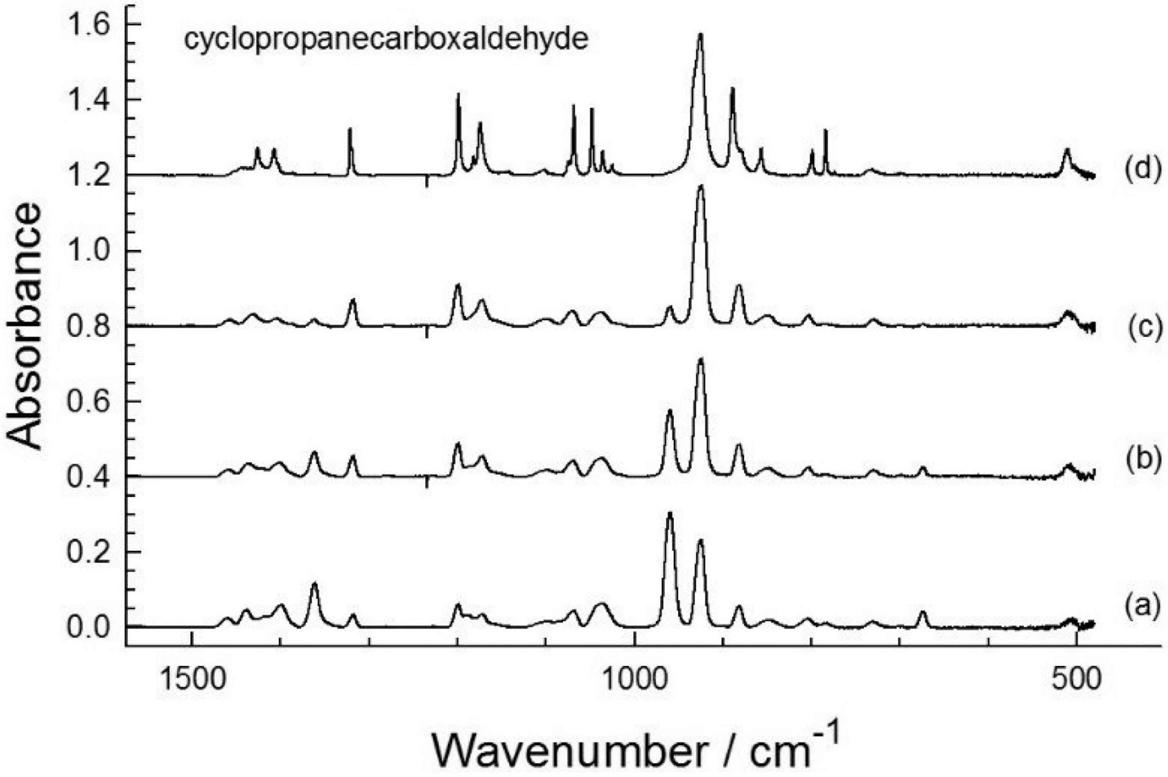


Figure 5.

Expansion of the IR fingerprint region of cyclopropanecarboxaldehyde. The ice was made at 13 K and its spectrum recorded at (a) 13 K, (b) 80 K, (c) 80 K after sitting at 80 K for ~18 hours, and (d) 140 K. The ice's thickness was about 2 μm.

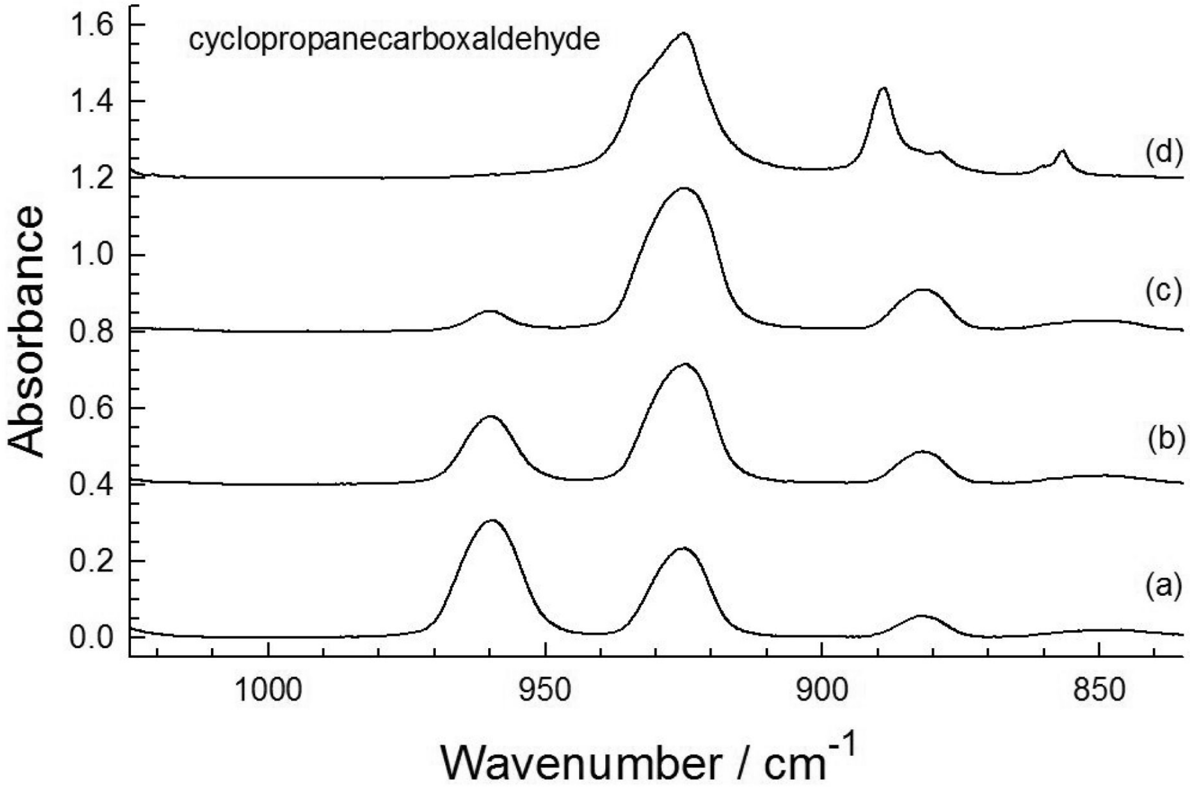


Figure 6.

Expansions of the IR spectra of Figure 5 to show *cis* and *trans* peaks of cyclopropanecarboxaldehyde near 959 and 925 cm^{-1}, respectively. The ice was made at 13 K and warmed as described in Figure 5.

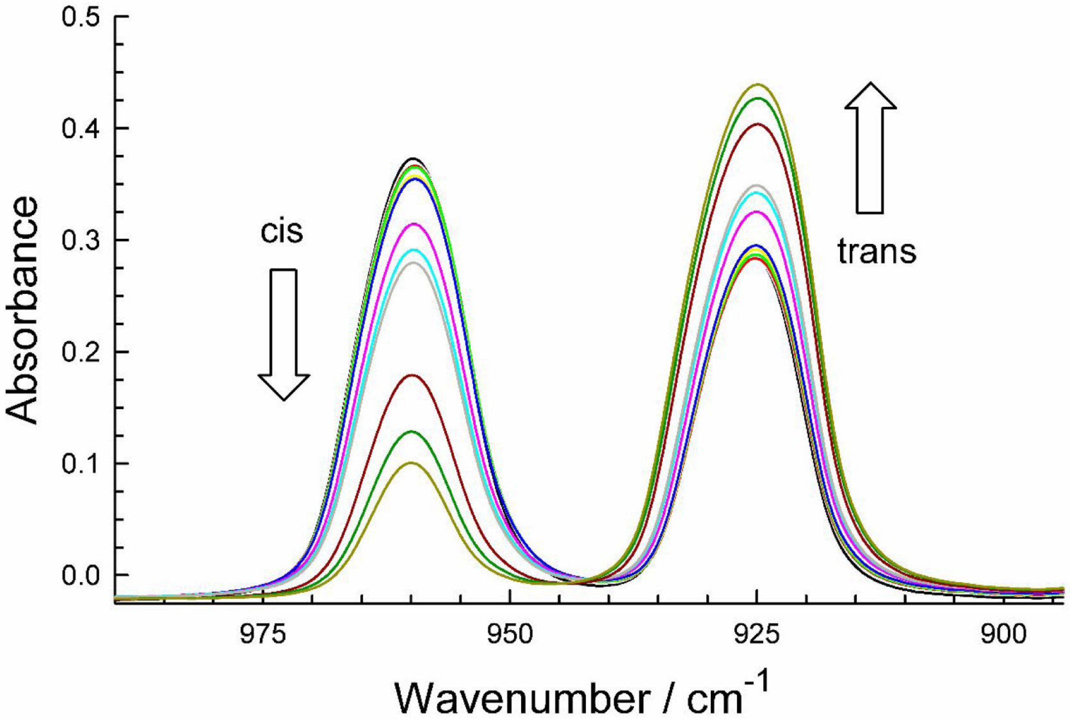


Figure 7.

Infrared spectra of cyclopropanecarboxaldehyde deposited at 14 K and then warmed to 85 K, showing the decrease in intensity for the peak of the *cis* isomer (left, 959 cm^{-1}), the increase in intensity of the peak for the *trans* isomer (right, 925 cm^{-1}), and an isosbestic point near 942 cm^{-1}.

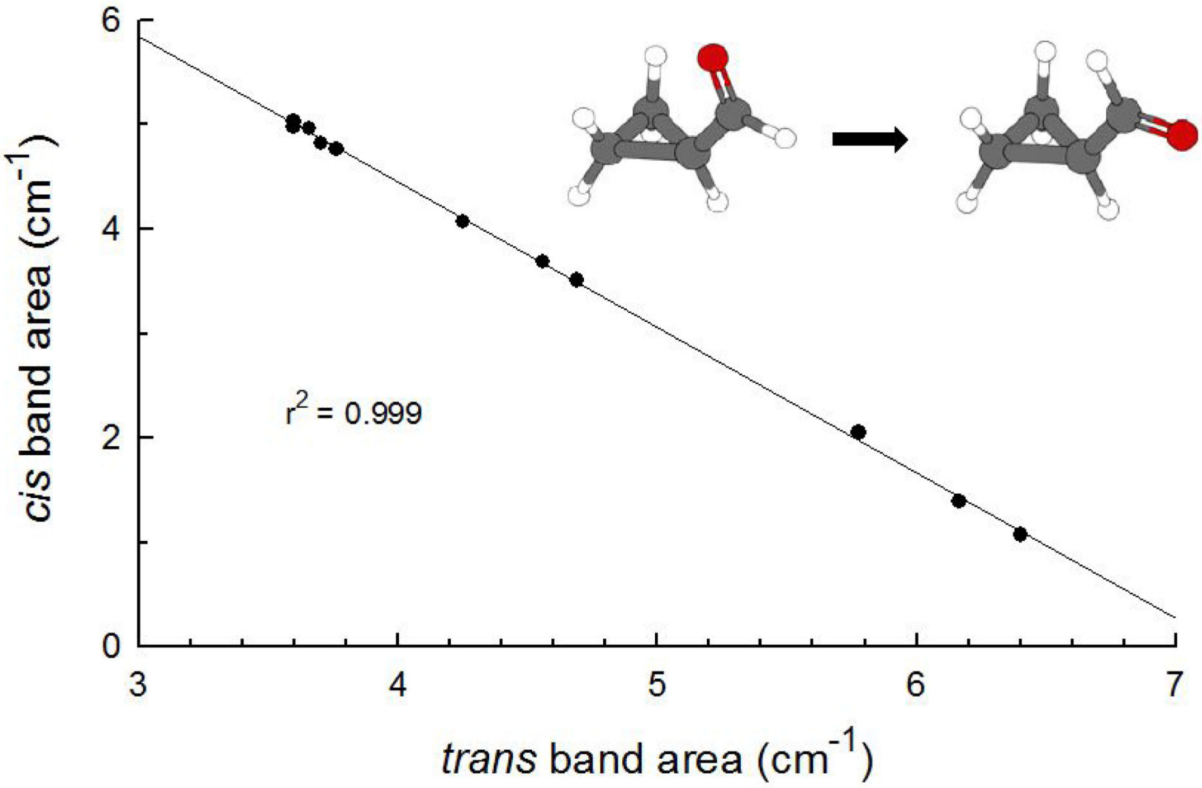


Figure 8.

Changes in areas for *cis* and *trans* bands of cyclopropanecarboxaldehyde near 959 and 925 cm^{-1}, respectively, as an amorphous sample was warmed from 14 to 80 K.

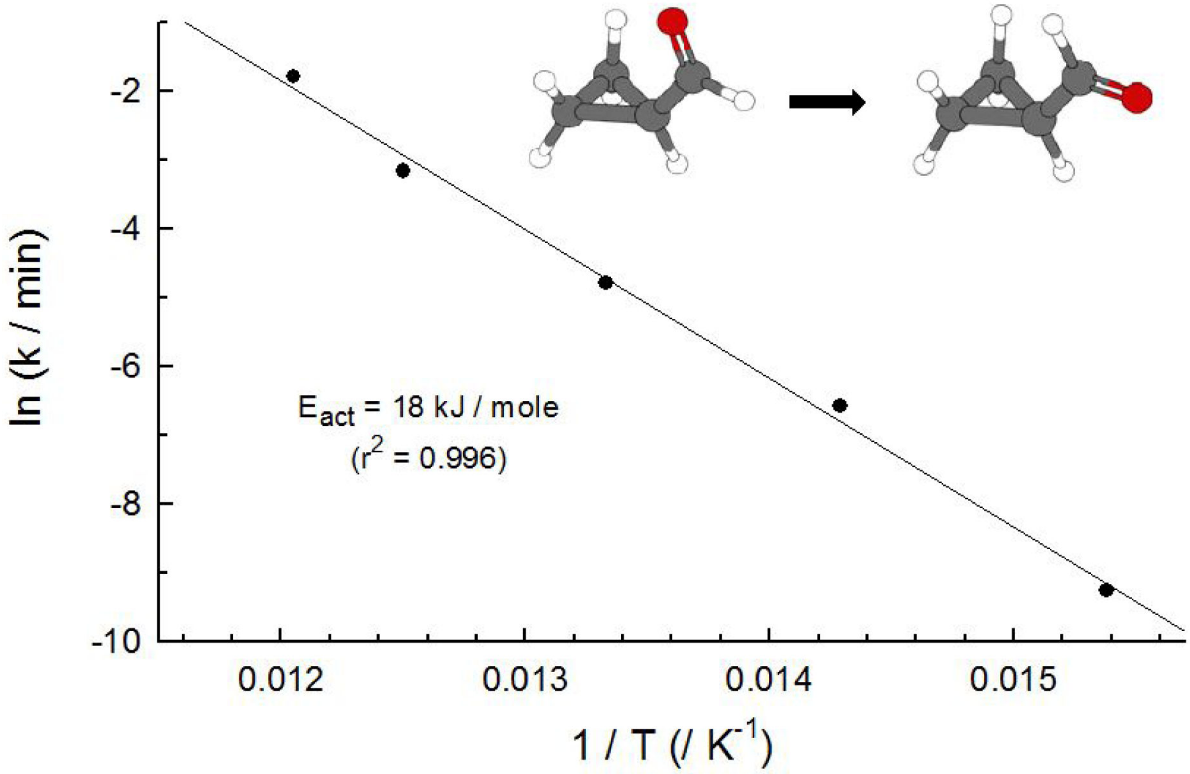


Figure 9.

Arrhenius plot for the *cis* → *trans* conversion of cyclopropylcarboxaldehyde.

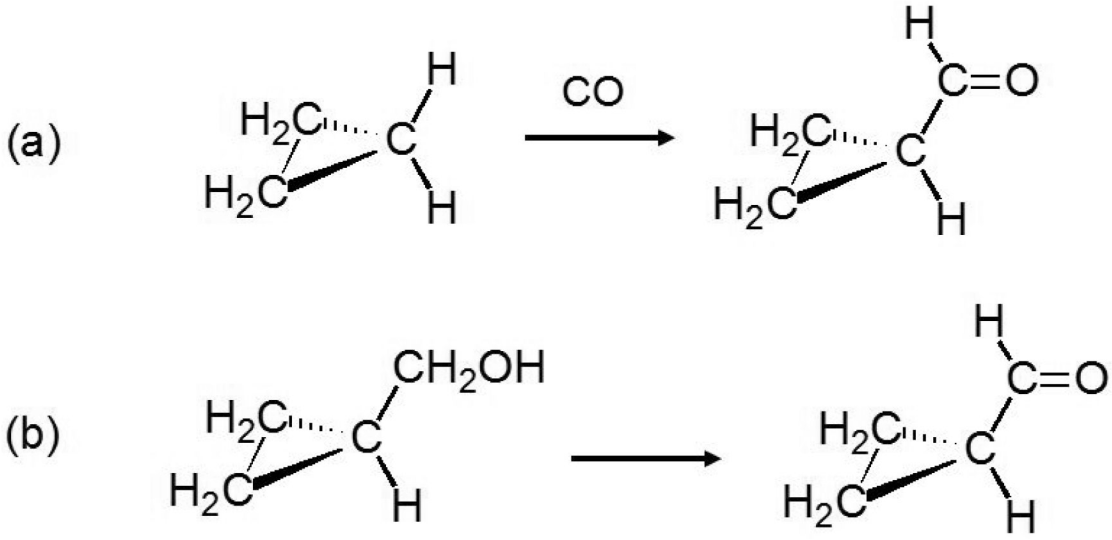


Figure 10.

Possible formation reactions for cyclopropanecarboxaldehyde by (a) synthesis involving cyclopropane and CO and (b) decomposition of cyclopropanemethanol.

Table 1 -

Refractive Indices and Densities for Three Amorphous Ices at 15 K

Property	***c*-C_3H_6**	***c*-C_3H_5-C(=O)H**	***c*-C_3H_5-CH_2OH**
n_{670}	1.416 ± 0.004	1.334 ± 0.003	1.311 ± 0.001
ρ (g cm^{-3})	0.774 ± 0.004	0.791 ± 0.004	0.696 ± 0.003
M (g mol^{-1})	42.08	70.09	72.11
ρ_N (molec cm^{-3})	1.108×10^{22}	6.792×10^{21}	5.815×10^{21}
r (cm^3 g^{-1})	0.324	0.261	0.278
R_M (cm^3 mol^{-1})	13.65	18.28	20.03

Table 2 –

Isomerization of Cyclopropanecarboxaldehyde

T / K	Time at T / hours	fraction *cis*	fraction *trans*
14	0.3	0.50	0.50
35	0.3	0.50	0.50
50	0.3	0.50	0.50
50	16.5	0.49	0.51
60	0.5	0.48	0.52
60	1.0	0.48	0.52
70	0.25	0.41	0.59
70	0.50	0.37	0.63
70	1.0	0.35	0.65
70	20	0.20	0.80
80	0.25	0.14	0.86
80	0.50	0.11	0.89