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Introduction

Although transition metal assisted catalytic processes/reactions in interstellar space were proposed long ago,¹ they have received consistent attention only in recent years.^{2,3} Our knowledge of transition metal assisted catalysis is largely derived from surface science experiments. Many such processes occur at a much higher temperature window than that is possible in the interstellar space. Mechanistic pathways involved in the catalysis for the formation of complex molecular species in the interstellar medium (ISM) and the role of transition metals in them are open questions. Considering the cryogenic conditions present in ISM, this catalysis reaction can be termed as "cryo-catalysis in ISM", which may be of much importance and can have great relevance in various astrochemical environments. Elements having atomic masses

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Iron assisted formation of CO₂ over condensed CO and its relevance to interstellar chemistry[†]

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Catalytic conversion of CO to CO_2 has been investigated in ultrahigh vacuum (UHV) under cryogenic conditions (10 K). This cryogenic oxidation is assisted by iron upon its co-deposition with CO, on a substrate. The study shows that the interaction of Fe and CO results in a Fe–CO complex that reacts in the presence of excess CO at cryogenic conditions leading to CO_2 . Here, the presence of CO on the surface is a prerequisite for the reaction to occur. Different control experiments confirm that the reaction takes place in the condensed phase and not in the gas phase. Surface sensitive reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD), and Cs⁺ based low energy ion scattering are utilized for this study. The iron assisted formation of CO_2 may be proposed as another pathway relevant in interstellar ices, containing CO. This direct oxidation process, which occurs at extremely low temperatures and pressures, in the presence of a reactive metal species like iron (the most abundant metal in the interstellar medium) may have astrochemical importance. It does not require any external energy in the form of photo-irradiation or thermal processing. Such reactions are highly relevant in cold dense molecular clouds where interactions between neutral species are more favoured.

greater than silicon are found in places like protostars, starforming regions, and even in diffused and cold dense clouds.^{4,5} Among these, iron is observed with higher abundance compared to several other transition metals^{5,6} and in fact, iron is the most abundant metal in the universe. These metals are produced and ejected as dust during star formation as well as during the death of stars.⁷ Considering the higher abundance of iron in ISM, the possibility of iron assisted catalysis is expected in these conditions.

Iron is known to be a well-known catalyst for the oxidation of CO to CO₂.⁸⁻¹¹ In the interstellar space, CO and CO₂ have been detected in various environments.^{12,13} However, the formation of CO₂ in the gas phase is not efficient to account for its proposed and observed abundance.14 Several pathways toward the formation of CO_2 in the interstellar space are proposed, such as UV photo-processing of CO ice, high energy ion irradiation of CO ice, oxygenation of CO ice, etc. 15-18 Formation of solid CO_2 has also been proposed through CO + O, CO + OH, and H₂CO + O routes.¹⁹⁻²¹ CO is ubiquitous in the ISM and its observed abundance can be explained by the gas phase reactions.²² In surface science literature, the interaction of CO with iron atoms and iron surfaces is well-studied.^{10,11,23} It is one of the model systems, understood in detail with respect to metal-ligand bond formation. CO can undergo dissociative adsorption on iron surfaces.8,9 Laser ablated iron oxides (clusters) react with CO to produce the carbonyl iron



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oxides $FeO(CO)_n$ (n = 1-3) and $FeO_2(CO)_m$ (m = 1, 2) which can further dissociate to give CO_2 ; such processes have been investigated using infrared spectroscopy.^{24,25} Besides, CO adsorbed on Fe(110) surface undergoes dissociation, and further oxidation in the presence of O_2 leads to CO_2 at room temperature and at higher temperatures.^{8,9,26}

In this work, we have studied the interaction of neutral iron atoms with CO, which is also abundantly found in ISM.¹³ The co-deposition of Fe and CO resulted in Fe + CO complex together with a small amount of CO₂. The observed CO₂ is a product formed due to the reaction of CO with iron atoms as we did not observe any CO₂ peak during the deposition of CO on the substrate. The Fe + CO band is broad in nature due to the formation of Fe(CO)_x (where x = 1-5).

The experiments were performed in simulated astrophysical conditions by depositing CO and iron atoms on a surface precooled to 10 K. The formation of CO_2 was observed just after the deposition, at 10 K. From different control experiments, it was concluded that the formation of CO_2 occurs on the surface, only in the presence of condensed CO and below the CO residence temperature. To further understand, we have performed a detailed DFT computational study on the electronic structure and vibrational frequency of Fe + CO complexes. The computed vibrational frequency of CO had been compared with our experimental frequency. We have also constructed a free energy map for the formation of CO_2 from the Fe + CO mixture. The proposed reaction mechanism justified the conversion of CO to CO_2 in the presence of Fe atoms.

Experimental

The experiments were performed in a custom-built ultrahigh vacuum instrument with a base pressure of $< 5 \times 10^{-10}$ mbar. A detailed description of the instrument is given elsewhere.²⁷ The instrument consists of a Ru(0001) substrate, where the molecular solids or ices are deposited. The substrate is attached to a 10 K closed-cycle helium cryostat with a copper holder. The temperatures are measured using a silicon diode sensor, a thermocouple sensor, and a Pt-sensor attached at three different points and are calibrated with ± 0.1 K accuracy. Molecular solid's structure, reactivity, etc., can be probed using several spectroscopic probes attached to the instrument chamber.²⁸⁻³¹ In this study, we used reflection absorption infrared (RAIR) spectroscopy and Cs⁺ based low energy ion scattering to probe the surface species and temperature programmed desorption (TPD) to examine the desorbed species. The background pressure before starting the experiment was maintained at $< 5 \times 10^{-10}$ mbar. We have deposited CO, iron, and the mixture (Fe + CO) on the pre-cooled Ru(0001) substrate at 10 K. CO gas (99.999% purity, RANA GAS) was leaked through an all-metal leak valve and metallic iron was evaporated using an electron beam evaporator (Mantis Deposition, e-beam evaporator). The electron beam evaporator can control the rate of evaporation by monitoring the deposition flux, via the ion current of the evaporant. The electron beam evaporator consists of an iron rod (99.99%, GoodFellow Cambridge Limited) which was placed

inside a tungsten crucible and heated using the electron beam, and the flux of the evaporant was monitored using a flux plate electrically isolated and biased at 50 V. We maintained the iron flux current at 3 nA (corresponding to ionized Fe atoms over the crucible) during deposition. The amount of iron atoms vaporized is proportional to the flux current. Nearly all the iron ions are neutralized at the flux plate, and no iron ions are falling on the substrate as no current was measured at the substrate. The thermal evaporator was kept 2 cm away from the substrate during the deposition of iron atoms and there was no increase in substrate temperature due to the evaporator. The UHV chamber was backfilled at 1×10^{-7} mbar of CO (by opening the all-metal leak valve) and was exposed to the surface for 10 minutes which would generate 50 MLs of solid CO on the substrate.²⁷ The deposition of Fe with 3 nA current (observed on the flux plate) for 10 minutes can give iron atoms of a few monolayers. In different experiments, we have maintained the above ratio of iron (3 nA) and CO (pressure at 1×10^{-7} mbar), constant. This constant ratio ensured that the experiments are similar, and the results could be compared with each other. The mixture (Fe + CO) was generated by switching on the evaporator and exposing the chamber with CO gas at 1 \times 10⁻⁷ mbar simultaneously. The simultaneous exposure for 10 minutes will lead to iron atoms getting mixed with CO in the gas phase and this mixture was getting deposited slowly on to the precooled Ru(0001) substrate to give multilayers of Fe + CO mixture. This thicker sample mixture (Fe + CO) makes sure that the Ru(0001) substrate does not have any influence on the reaction. We have also performed sequential deposition, where CO gas was backfilled for 10 minutes, followed by Fe (3 nA for 10 minutes) by giving a time gap in between for the background pressure to come down to the initial values.

To confirm further that the substrate is not affecting the reaction, solid argon and later water-ice (both amorphous and crystalline forms of ice) were used to cover the ruthenium substrate. Argon (99.998%, Sigma Aldrich) was used at a pressure (back-filling the chamber) of 5 \times 10^{-7} mbar for 16 minutes to produce ~ 500 MLs coverage. H₂O (99.996%, Millipore), taken in a glass to metal seal adaptor, further purified by several freeze pump thaw cycles, was used to deposit water-ice. Amorphous ice was grown by depositing water vapor by backfilling the chamber at 1×10^{-7} mbar pressure for 16.7 minutes, to give ~ 100 MLs of amorphous ice at 10 K. Crystalline ice was developed by depositing the same amount of water vapor at 120 K, further heated to 145 K and subsequently cooled back to 10 K. A residual gas analyser (RGA) was run throughout the deposition which ensured the purity of the gas getting deposited.

After deposition, the deposited sample was heated resistively, and the substrate temperatures were controlled by a LakeShore temperature controller. A typical RAIR spectrum was collected as an average of 512 scans. Temperature-dependent RAIR spectra were measured by depositing Fe + CO mixtures at 10 K and subsequently heating them to higher temperatures at 2 K min⁻¹ heating rate and giving a 2 minute equilibration time after reaching the desired temperature, followed by spectral measurement.

Computational quantum chemistry, especially DFT, is well suited for understanding the mechanistic insights of transitionmetal-catalysed chemical reactions by providing detailed reaction energy profiles with the geometric and electronic structures of reactants, products, intermediates, and transition states. Singlepoint DFT calculations, similar to previously performed computational analyses of metal clusters,³² were likewise carried out *via* the Gaussian 09 computational package.³³ In this study, we chose 6-31+G^{*}, a double- ζ Popletype basis set. LANL2DZ (Los Alamos National Laboratory 2 double- ζ), which is a widely used, effective core potential (ECP)-type basis set, was used to model the metal atoms.³³ This mixed basis set was created through the use of the GEN keyword in Gaussian 09.

Frequency analysis was performed on each ground state and transition state. We verified that all frequencies are positive for each ground state, and only one imaginary frequency existed (within a computational tolerance of 30 cm^{-1}) for each transition state complex. It has been shown that the current DFT method (with B3LYP functional) provides reliable geometries, energies, and vibrational frequencies in related mechanistic studies.³⁴

Results and discussion

The experiment was carried out by depositing CO on a precooled Ru(0001) substrate at 10 K. Subsequently, in a different experiment, CO was deposited along with iron atoms. Fig. 1 shows the RAIR spectrum obtained upon depositing CO at 10 K (bottom trace) and upon co-deposition of CO along with iron (Fe + CO) (top trace) at 10 K. The spectra are shown in a range focussing on the C=O antisymmetric stretching band (2142 cm⁻¹). Solid pure CO shows a C=O stretching peak at



Fig. 1 RAIR spectrum collected upon deposition of CO on top of Ru(0001) substrate (Ru@CO) (bottom trace) and co-deposition of thermally evaporated iron with CO (Ru@Fe + CO) at 10 K (top trace). The CO₂ peak obtained at 2343 cm⁻¹ is multiplied by a factor of 20. Peak labeled * is due to the ¹³CO.

2142 cm⁻¹ and a small peak at 2092 cm⁻¹ arises due to the contribution from ¹³CO molecules,¹⁸ present with ¹²CO as a natural impurity. When CO was deposited along with iron atoms, we observed three peaks, (i) CO antisymmetric stretching peak (2142 cm⁻¹) with reduced intensity compared to the pure sample, (ii) a broad band in the 2100 to 2000 cm⁻¹ range, attributed to the formation of an Fe + CO complex and (iii) a weak peak at 2343 cm⁻¹ due to the antisymmetric (C=O) stretching mode of CO₂.

During the deposition, iron can interact with more than one CO molecules to form a range of $Fe(CO)_x$ clusters. The C==O stretching positions will be different for all the various combinations of Fe and CO. Previous reports suggest that both thermally evaporated iron atoms, as well as laser-ablated iron atoms, form $Fe(CO)_x$ clusters upon reaction with CO in the gas phase.^{35,36} The infrared peaks of these $Fe(CO)_x$ were already reported in the literature by depositing them in various matrices.^{37,38}

Computationally, we calculated the optimized vibrational frequencies for CO, CO₂, and Fe(CO)_{*x*} (x = 1-5) complexes. The calculated IR frequencies of the CO and Fe(CO)_{*x*} are compared with the experimental IR frequencies, as shown in Fig. S1 (ESI†). The experimental and calculated spectra are qualitatively similar. Our DFT calculations predicted that the C==O stretching frequency for Fe(CO)_{*x*} complex shows a lower wavenumber value (red-shift) with respect to free CO.

In order to characterise the Fe + CO mixture, temperaturedependent RAIRS measurement of the same was performed by slowly heating the substrate from 10 K to higher temperatures and measuring the RAIR spectrum at each temperature indicated, as shown in Fig. 2a. Enlarged regions from Fig. 2a corresponding to CO_2 and $Fe(CO)_x$ regions are shown in the insets as Fig. 2b and c, respectively. The CO₂ region is multiplied by a factor of 10 for better visibility. The intensity of the C=O stretching peak (2142 cm^{-1}) goes down completely above 30 K, attributed to CO desorption, whereas the broad $Fe(CO)_x$ band stayed till 250 K but its intensity got reduced above 150 K. $Fe(CO)_x$ may undergo dissociative desorption upon heating, and it was completely dissociated at ~ 250 K. However, this happens very slowly with temperature. This implies that the $Fe(CO)_r$ cluster has higher desorption energy. Fig. 2b shows the characteristic peak of solid CO_2 (2342 cm⁻¹), which eventually gets desorbed above 80 K, in accordance with the desorption temperature of CO₂ in UHV.³⁹

Low energy Cs⁺ collision was also performed on the deposited Fe + CO mixture to check the species formed due to the reaction. These data are shown in Fig. 2d and e. Cs⁺ scattering is a versatile surface analytical technique and is very specific to the top few layers.^{40,41} Low energy (~40 eV) Cs⁺ upon collision on the surface undergoes reactive ion scattering where Cs⁺ picks up the surface molecules forming an adduct-ion species, which can be detected by a mass spectrometer. During 40 eV Cs⁺ collision (Fig. 2d), Cs-CO⁺ (m/z = 161) was observed as the major peak next to Cs⁺ (m/z = 133) and Cs-CO₂⁺ (m/z = 177) as a minor peak, confirming the presence of CO₂ molecules on the surface. Upon increasing the kinetic energy of Cs⁺ to 80 eV (Fig. 2e), various peaks related to



Fig. 2 (a) Temperature-dependent RAIR spectra of Fe + CO deposited mixture. The insets (b) and (c) are enlarged views of the CO_2 and $Fe(CO)_x$ regions, respectively. Figures (d) and (e) are the Cs^+ scattering spectra of Fe + CO deposited mixture at 40 eV and 80 eV ion kinetic energy, respectively. Various features are marked. The mixture was deposited, and the scattering spectra were collected at 10 K.

Fe(CO)_{*x*} and Fe started to appear. The relatively higher energy of Cs⁺ (~80 eV) makes it act mainly as a sputtering source and the deeper monolayers will be probed after knocking out the molecules from the top surface. At higher collision energies of Cs⁺, the product ions (Cs-CO₂⁺, in our case) can also dissociate, explaining the observations. These data suggest that Fe(CO)_{*x*} consists of various combinations of CO bound with iron and the value of *x* can be from 1 to 5.

The Fe + CO deposited mixture was further characterised by temperature programmed desorption (TPD). The obtained TPD spectra of the Fe + CO mixture is shown in Fig. S2a (ESI[†]). In this experiment, the deposited Fe + CO mixture was heated from 10 K, at a heating rate of 30 K min⁻¹. The intensity of the desorbed species of masses 28 (for CO) and 44 (for CO₂) were plotted as a function of substrate temperature. TPD spectra of mass 28 (Fig. S2a, ESI[†]) shows the characteristic peak centered at \sim 30 K, due to the desorption of CO molecules having weak or no interaction with Fe atoms. The observed tail, which continued above 120 K, originated from the CO molecules interacting with the Fe atoms and also from the dissociation of $Fe(CO)_x$. Such a dissociation of $Fe(CO)_5$ upon chemical vapor deposition is already reported at higher temperatures.⁴² TPD of mass 44 gave a peak centered at 85 K, which is the characteristic desorption profile of CO2.39 This is very low in intensity and is shown in the inset (Fig. S2b, ESI⁺). Fig. S2c (ESI⁺) is the instantaneous mass spectrum obtained at 85 K showing the intensity ratios of CO_2^+ and CO^+ along with C^+ and O^+ .

The gas-phase reactions of CO molecules with Fe atoms are highly feasible, leading to $Fe(CO)_x$.^{35,37,38} In order to observe whether the reaction is occurring in the gas phase or the

condensed phase and to get a better insight into the formation mechanism of CO_2 , different control experiments were carried out. The Fe + CO mixture was deposited at various temperatures (10 K, 20 K, 30 K, 40 K, 50 K and 60 K). These data are shown in Fig. 3a. Since the desorption temperature of CO is 30 K, the possibility of CO molecule to get deposited above 30 K in the Fe + CO mixture is negligible. The primary observation upon deposition of Fe + CO at various temperatures is that the formation of CO_2 solely depends on the residence of CO at the surface.

We have also calculated the column densities of CO and CO₂ formed at various temperatures from Fig. 3a and the results are plotted together in Fig. 3b. Major observations from the data can be summarized as, (i) the formation of CO_2 decreases substantially with increase in the deposition temperature and follows the column density pattern of CO. Maximum formation of CO₂ was observed when Fe and CO were co-deposited at 10 K. (ii) There is a drastic decrease of CO_2 peak intensity above 30 K, which is the temperature above which CO will not get condensed on the surface. This led us to suggest that an excess or unbound CO molecule is required for the iron assisted CO2 formation. (iii) The formation of CO₂ stops completely at and above 50 K. This observation suggests that the reaction is occurring in the condensed phase only, and the possibility of the same in the gas phase can be ruled out. If the reaction is feasible in the gas phase, it must have formed at all the above temperatures and the formed CO₂ must have condensed till 80 K, since CO₂ is known to desorb only above 80 K. A small amount of CO₂ was observed at 40 K. It may be explained as follows: CO gets dissociated from $Fe(CO)_x$ and is also available



Fig. 3 (a) Iron and CO co-deposited at various temperatures (10-60 K). (b) The column density ratios of CO and CO₂ calculated from the data obtained from the experiments depositing Fe + CO at different temperatures.

from trapped CO, which gets desorbed at a higher temperature than its usual desorption temperature (30 K).^{43,44} The trapped CO was observed as a tail in the TPD profile of the CO desorption curve in the Fe + CO mixture in Fig. S2a (ESI[†]). The intensity of the tail reduces with temperature. Similar trapping of CO (of very less amount) is possible when we deposit Fe + CO at 40 K and we strongly believe that this trapped CO is making the formation of CO₂ feasible at 40 K. The intensity of CO₂ formed at 40 K is much lower than that at 30 K (Fig. 3b). Another observation is that the ratio of CO to CO2 intensity is also quite less for the 40 K deposition experiment (Fig. 3a). This may be due to an experimental limitation, which can be explained as follows: the formation of CO₂ from Fe + CO mixture is not time dependent. The desorption temperature of CO from different surfaces is higher than 30 K, and ranges up to 40 K.43-45 We measured the RAIR spectrum after the deposition of Fe + CO mixture (at 40 K) and waiting for the pressure to settle down to the base pressure. The 512 scans used in the spectral collection took around 7 minutes. Throughout this time, the surface was equilibrated at 40 K, which made a significant amount of CO to desorb leading to reduced intensity of CO than CO₂ (at 40 K). Above 40 K, upon deposition of the Fe + CO mixture, the chance of CO getting trapped decreased substantially as it was far above its desorption temperature which restricted the

formation of CO_2 completely as unbound surface CO was required for CO_2 formation.

It may be concluded from the above data that an excess or unbound CO in the condensed phase is essential for the formation of CO₂. The Fe–CO bond formation weakens the C–O bond resulting in partial dissociation of O. This partially dissociated O in Fe + CO can bind with a free CO molecule leading to CO₂ and the remaining part stays as iron carbide and the entire process occurs in the condensed phase.

The reaction can be explained by the following equations,

$$C \equiv O + Fe \rightarrow Fe - C \equiv O \tag{1a}$$

$$Fe-C \equiv O + C \equiv O \rightarrow Fe-C + O \equiv C \equiv O$$
 (1b)

The overall reaction mechanism consists of two molecules of CO getting converted to one molecule of CO_2 in the presence of a Fe atom. We have plotted the gas-phase Gibbs free energy (ΔG , kcal mol⁻¹) and the mechanism with reaction coordinate in Fig. 4.

The reaction mechanism begins with the formation of FeCO, a complex that is 2.73 kcal mol⁻¹ stable than the reactants. The preferred pathway continues through the insertion of one more CO molecule to form Fe(CO)₂. The intrinsic reaction coordinate (IRC) revealed that transition state (TS) is actually an O-transfer from one CO to other CO molecule, which occurs with a minimal activation barrier *via* TS (+4.65 kcal mol⁻¹). Transition states were confirmed by vibrational frequency calculations yielding a single imaginary frequency along the reaction coordinate. Consequently, the breakage of the C–O bond occurs, which leads to FeC–CO₂. The final step is the formation of free CO₂ and FeC. The data depicted in Fig. 3 could surely conclude that (i) the formation of CO₂ is highly dependent on the accessibility of free or unbound CO and (ii) the reaction happens in the condensed phase.

The current experiments could not resolve all the observations. For example, the deposition of Fe and CO mixture at 10 K and 20 K is observed to give almost the same intensity of CO (corresponds to the same amount of deposition) while the CO_2 formed at these two temperatures show a linear decrease.



Fig. 4 Proposed reaction mechanism for the formation of CO₂ from CO with Fe atom. The relative energies are given in kcal mol^{-1} .

The reason for this could not be explained. The computed mechanism (Fig. 4) serves well to explain our experimental observation, except the temperature dependence of the experiment, that more CO₂ was observed at 10 K. This could be because the ΔG values were computed for gas phase reactions and not considering condensed state of these species. We believe that this difference in the conditions of calculations and experiments is reflected in the discrepancy in the temperature dependence. However, the intermolecular interaction between CO and Fe will be similar in both gaseous and condensed phases. Literature reports^{46,47} suggest that disproportionation reactions as depicted in the mechanism could occur at low temperatures.

Role of substrate in the reaction

All these reactions described above were performed on a Ru(0001) substrate. In order to confirm that the substrate does not have any role in the present reactions, we covered the Ru(0001) substrate by depositing 500 MLs of argon. This was followed by co-deposition of Fe and CO mixture on top of argon. The result obtained was very similar (data are not shown), which makes us conclude that the reaction is substrate independent.

We also performed other sets of experiments by depositing iron on CO and also a reverse experiment; by depositing CO on iron sequentially, both at 10 K. The experiments were performed on Ru(0001) substrate as well as by covering it with 500 MLs of argon. The results were similar and the data

obtained upon deposition on argon covered Ru(0001) substrate are shown in Fig. 5a and b. Here, we observed the IR peak for CO2 (at 10 K) when iron was deposited on top of CO (Fig. 5a) while, a similar IR peak of CO₂ was not observed in the reverse case where CO was deposited on top of iron (Fig. 5b). The observation from Fig. 5 would lead us to suggest that heat of adsorption of iron atoms on solid CO is facilitating this reaction. Neutral iron atoms upon condensation on solid CO would react to give Fe-CO complex and CO₂. The observation that CO₂ was not formed above 40 K from the deposition of the species at various temperature experiment (Fig. 3) clearly confirms that this is a condensed phase reaction and more CO₂ formed at temperatures lower than 30 K suggests the presence of free or unbound CO is necessary for this (CO₂ formation) reaction to proceed. The above sequential deposition experiment of Fe atoms on solid CO could be more realistic or a better model for ISM but the product (CO₂) formed was less as compared to co-deposition experiment. We attribute this to the better interaction of Fe and CO possible in a co-deposition method than the sequential deposition. In sequential deposition, iron atoms could interact only with the surface CO molecules while in co-deposition, the interactions are more as CO and Fe are getting mixed during the deposition, which leads to more amount of CO₂ than the former. However, the observation of the formation of CO₂ in both cases predicts that the reaction proceeds in a very similar way in both cases.

To give more realistic data pertaining to the interstellar medium, we performed a similar experiment by depositing



Fig. 5 (a) RAIR spectra collected upon deposition of thermally evaporated iron on top of CO at 10 K. (b) Similar RAIR spectral measurement from the deposition of CO on top of deposited iron. The substrate was initially covered by 500 MLs of argon in order to avoid the interaction and any probable influence of the Ru(0001) substrate. The inset shows the schematic of the sample and the order of deposition. The spectra have corresponding labels. The CO₂ stretching region is enlarged and multiplied by a factor of 50 for better clarity. (c) RAIR spectra obtained from Fe + CO mixture co-deposited on amorphous and crystalline water at 10 K. The spectral regions of water, CO₂, CO, and Fe(CO)_x are labeled. The CO₂ antisymmetric stretching region is enlarged. The inset shows a schematic of the sequence of deposition of molecules under study.

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Fe + CO mixture on top of water-ice, both amorphous and crystalline forms. Amorphous ice was formed by depositing water at 10 K followed by Fe + CO deposition as mentioned before. Crystalline ice was developed by depositing water vapor at 120 K and heating the sample ice to 145 K. The crystalline ice sample was subsequently cooled to 10 K and Fe + CO was co-deposited on top. These data are shown in Fig. 5c. We could not find any additional peak due to water molecules interacting with CO or Fe atoms. However, the formation of CO_2 due to the interaction of Fe + CO occurs on the water surface at 10 K. Data from amorphous and crystalline ices also suggest this. The intensity of CO_2 formed is higher on amorphous ice than on the crystalline ice, although this result needs further investigation. Altogether, this proves that the Fe can react with condensed CO leading to CO_2 and this reaction could proceed on the water surface.

Conclusions

We performed co-deposition of CO and iron atoms on a substrate, pre-cooled to 10 K. Such a deposition gave peaks corresponding to pure CO at 2142 cm⁻¹, and a broad band in ~2000 cm⁻¹ range due to CO bonded with Fe [Fe(CO)_x] in the infrared spectrum. More importantly, a new peak due to CO₂ (2343 cm⁻¹) was observed due to the reaction. The Fe + CO solid mixture was further characterised by temperature-dependent RAIRS, low energy Cs⁺ scattering, and TPD, revealing that Fe(CO)_x is one in which *x* = 1 to 5. Infrared frequencies were calculated by optimizing different structures and was found to be matching with the experimentally obtained values. This Fe(CO)_x dissociates to give Fe and CO, which disappears completely above 250 K.

The formation of CO₂ is an instantaneous process upon the deposition of iron atoms on CO (or during co-deposition) and was found to proceed only in the presence of unbound CO, as proven by different control experiments. Based on these experiments, we propose that iron assisted formation of CO_2 is another pathway that can occur in interstellar ices containing condensed CO. The importance of this reaction is that it is a direct oxidation of CO to CO_2 at cryogenic temperatures, made possible by a reactive metal species like iron being condensed on the molecular surface. It does not require any form of photo-irradiation or thermal processing and occurs at lower temperatures (such as 10 K). Such a reaction is a highly favorable one in cold dense molecular clouds where the presence of CO and Fe are detected in abundance. The reaction occurs also on the surface of water ice and CO₂ was detected in more abundance on amorphous ice. Mechanistic details of the CO2 formation reaction were supported by computational studies.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 D. K. Bohme, Chem. Rev., 1992, 92, 1487-1508.
- 2 M. Fioroni, Phys. Chem. Chem. Phys., 2014, 16, 24312-24322.
- 3 M. Fioroni, Comput. Theor. Chem., 2016, 1084, 196-212.
- 4 M. J. Adrienne, S. S. Norbert, C. Deepto and W. G. Thomas, *Astrophys. J.*, 2006, **648**, 1066.
- 5 C. M. Walmsley, R. Bachiller, G. Pineau des Forets and P. Schilke, *Astrophys. J.*, 2002, **566**, L109–L112.
- 6 A. P. Jones, Mon. Not. R. Astron. Soc., 1990, 245, 331-334.
- 7 P. Ventura, M. Di Criscienzo, R. Schneider, R. Carini, R. Valiante, F. D'Antona, S. Gallerani, R. Maiolino and A. Tornambe, *Mon. Not. R. Astron. Soc.*, 2012, 420, 1442–1456.
- 8 D. E. Jiang and E. A. Carter, Surf. Sci., 2004, 570, 167-177.
- 9 T. Wang, X.-X. Tian, Y.-W. Li, J. Wang, M. Beller and H. Jiao, *ACS Catal.*, 2014, **4**, 1991–2005.
- 10 Y.-H. Chen, D.-B. Cao, J. Yang, Y.-W. Li, J. Wang and H. Jiao, *Chem. Phys. Lett.*, 2004, **400**, 35–41.
- 11 S. K. Nayak, M. Nooijen, S. L. Bernasek and P. Blaha, J. Phys. Chem. B, 2001, 105, 164–172.
- 12 L. B. D'Hendecourt and M. Jourdain de Muizon, *Astron. Astrophys.*, 1989, **223**, L5–L8.
- 13 A. G. G. M. Tielens, A. T. Tokunaga, T. R. Geballe and F. Baas, Astrophys. J., 1991, 381, 181–199.
- 14 E. F. Van Dishoeck, F. P. Helmich, T. De Graauw, J. H. Black, A. C. A. Boogert, P. Ehrenfreund, P. A. Gerakines, J. H. Lacy and T. J. Millar, *et al.*, *Astron. Astrophys.*, 1996, 315, L349–L352.
- 15 C. J. Bennett, C. S. Jamieson and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4032–4050.
- 16 S. Ioppolo, M. E. Palumbo, G. A. Baratta and V. Mennella, *Astron. Astrophys.*, 2009, **493**, 1017–1028.
- 17 H. Linnartz, S. Ioppolo and G. Fedoseev, Int. Rev. Phys. Chem., 2015, 34, 205–237.
- 18 M. J. Loeffler, G. A. Baratta, M. E. Palumbo, G. Strazzulla and R. A. Baragiola, *Astron. Astrophys.*, 2005, **435**, 587–594.
- 19 M. Minissale, E. Congiu, G. Manicò, V. Pirronello and F. Dulieu, *Astron. Astrophys.*, 2013, **559**, A49.
- 20 M. Minissale, J.-C. Loison, S. Baouche, H. Chaabouni, E. Congiu and F. Dulieu, *Astron. Astrophys.*, 2015, 577, A2.
- 21 J. A. Noble, F. Dulieu, E. Congiu and H. J. Fraser, Astrophys. J., 2011, 735, 121.
- 22 P. M. Solomon and W. Klemperer, Astrophys. J., 1972, 178, 389–421.
- 23 A. Stibor, G. Kresse, A. Eichler and J. Hafner, *Surf. Sci.*, 2002, 507–510, 99–102.
- 24 Z.-H. Lu and Q. Xu, J. Chem. Phys., 2011, 134, 034305.
- 25 W. Xue, Z.-C. Wang, S.-G. He, Y. Xie and E. R. Bernstein, J. Am. Chem. Soc., 2008, 130, 15879–15888.
- 26 S. Liu, Y.-W. Li, J. Wang and H. Jiao, J. Phys. Chem. C, 2015, 119, 28377–28388.

- 27 S. Bag, R. G. Bhuin, R. R. J. Methikkalam, T. Pradeep, L. Kephart, J. Walker, K. Kuchta, D. Martin and J. Wei, *Rev. Sci. Instrum.*, 2014, 85, 014103.
- 28 J. Ghosh, R. G. Bhuin, G. Ragupathy and T. Pradeep, J. Phys. Chem. C, 2019, 123, 16300–16307.
- 29 J. Ghosh, A. K. Hariharan, R. G. Bhuin, R. R. J. Methikkalam and T. Pradeep, *Phys. Chem. Chem. Phys.*, 2018, **20**, 1838–1847.
- 30 J. Ghosh, R. R. J. Methikkalam, R. G. Bhuin, G. Ragupathy, N. Choudhary, R. Kumar and T. Pradeep, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 1526–1531.
- 31 J. Ghosh, R. G. Bhuin, G. Vishwakarma and T. Pradeep, J. Phys. Chem. Lett., 2020, 11, 26–32.
- 32 E. G. Mednikov, S. A. Ivanov and L. F. Dahl, *Inorg. Chem.*, 2011, **50**, 11795–11806.
- 33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi,

- J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09 Rev. A.1*, Wallingford, CT, 2009.
- 34 Y. Yang, M. N. Weaver and K. M. Merz, J. Phys. Chem. A, 2009, 113, 9843–9851.
- 35 C. H. F. Peden, S. F. Parker, P. H. Barrett and R. G. Pearson, J. Phys. Chem., 1983, 87, 2329–2336.
- 36 M. Zhou, L. Andrews and C. W. Bauschlicher, *Chem. Rev.*, 2001, **101**, 1931–1962.
- 37 M. Zhou and L. Andrews, J. Chem. Phys., 1999, 110, 10370-10379.
- 38 M. Zhou, G. V. Chertihin and L. Andrews, J. Chem. Phys., 1998, 109, 10893–10904.
- R. M. Escribano, G. M. Muñoz Caro, G. A. Cruz-Diaz,
 Y. Rodríguez-Lazcano and B. Maté, *Proc. Natl. Acad. Sci.* U. S. A., 2013, 110, 12899–12904.
- 40 H. Kang, Acc. Chem. Res., 2005, 38, 893-900.
- 41 H. Kang, Bull. Korean Chem. Soc., 2011, 32, 389-398.
- 42 F. Zaera, Langmuir, 1991, 7, 1188-1191.
- 43 S. Cazaux, R. Martín-Doménech, Y. J. Chen, G. M. M. Caro and C. G. Díaz, *Astrophys. J.*, 2017, 849, 80.
- 44 J. A. Noble, E. Congiu, F. Dulieu and H. J. Fraser, Mon. Not. R. Astron. Soc., 2012, 421, 768–779.
- 45 S. E. Bisschop, H. J. Fraser, K. I. Öberg, E. F. van Dishoeck and S. Schlemmer, *Astron. Astrophys.*, 2006, **449**, 1297–1309.
- 46 H. J. Lee and W. Ho, Science, 1999, 286, 1719-1722.
- 47 J. R. Hahn and W. Ho, Phys. Rev. Lett., 2001, 87, 166102.