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# Experimental studies of surface reactions among OH radicals that yield H<sub>2</sub>O and CO<sub>2</sub> at 40–60 K

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We investigated the OH-related formation routes of two astrophysically important molecules, H<sub>2</sub>O and CO<sub>2</sub>, under relatively warm astrophysical conditions. OH radicals, together with other neutral species such as H, O, H<sub>2</sub>, and O<sub>2</sub>, were produced in H<sub>2</sub>O microwave-discharge plasma and cooled to 100 K before being deposited on an Al substrate at 40–60 K. H<sub>2</sub>O formed at 40 and 50 K, but not at 60 K. Taking the experimental conditions into account, a possible route of H<sub>2</sub>O formation is via reactions involving OH + OH, which yield H<sub>2</sub>O<sub>2</sub> as the main reaction product. The present study is the first to show experimentally that surface reactions of two OH radicals can yield H<sub>2</sub>O at low temperatures. The products' branching ratio was 0.2 and 0.8 for H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, respectively. When CO was co-deposited with neutral species that formed in the H<sub>2</sub>O plasma, CO<sub>2</sub> was formed at 40–60 K. H<sub>2</sub>CO<sub>3</sub> formed at 40 and 50 K. The present results may suggest that chemical reactions related to OH radicals are effective at yielding various molecules in relatively warm astrophysical environments, such as protostars.

## 1 Introduction

It has been demonstrated theoretically that hydroxyl (OH) radicals are related to various chemical reactions that occur on solid surfaces in astrophysical environments.<sup>1,2</sup> It is also well known that OH radicals play a significant role in photon-induced chemical reactions involving H<sub>2</sub>O ices, because they are easily produced by the photolysis of solid H<sub>2</sub>O at various temperatures.<sup>3–5</sup> Previous experiments demonstrated experimentally that chemical reactions induced by UV photons in astrophysically relevant ices can yield various complex species.<sup>6,7</sup> In those experiments, various reactions may occur due to energy input from photons, even if they are highly endothermic and have large activation barriers. In contrast, nonenergetic surface reactions are simple and suitable for understanding the elementary process of radical–molecule reactions. In our previous studies, nonenergetic OH radicals were obtained by dissociating H<sub>2</sub>O in microwave-induced plasma, followed by cooling to 100 K before the reaction.<sup>8,9</sup> Therefore, we are able to investigate the OH-related formation pathways of various molecules under astrophysically relevant conditions.

Solid H<sub>2</sub>O is ubiquitous in icy grain mantles in dense molecular clouds.<sup>10</sup> Previous studies have demonstrated experimentally that solid H<sub>2</sub>O can be formed at ~10 K by the sequential addition of H to O,<sup>11,12</sup> O<sub>2</sub>,<sup>13,14</sup> or O<sub>3</sub>.<sup>15,16</sup> Cup-

pen et al.<sup>17</sup> recently proposed that hydrogen addition to HO<sub>2</sub> radicals can also yield H<sub>2</sub>O on a low-temperature surface. Although H<sub>2</sub>O formation routes involving atomic H have been extensively investigated experimentally, few studies have focused on OH-related formation routes of H<sub>2</sub>O under astrophysically relevant conditions. In fact, OH radicals should form as an intermediate species during the sequential addition of H to O, O<sub>2</sub>, or O<sub>3</sub>.<sup>18</sup> However, OH-related routes cannot be distinguished from other H<sub>2</sub>O formation routes that have been shown to occur concurrently under experimental conditions.<sup>11–16</sup> For example, Dulieu et al.<sup>12</sup> investigated reactions of atomic D (instead of H) with atomic O. In their experiment, atomic O was obtained by dissociating molecular O<sub>2</sub> with a dissociation efficiency of ~40%, which means that ~60% of molecular O<sub>2</sub> remained nondissociated and, therefore, could react with D. Although they estimated the efficiency of the O + D (OD + D) reaction from the temperature-programmed desorption spectra of the reaction products, the latter were not monitored in situ; no direct evidence was presented for the efficiency of the reaction. Therefore, if the OH-related formation routes of H<sub>2</sub>O are understood in terms of their efficiency, the chemical-reaction network under astrophysically relevant conditions can be better understood.

Carbon dioxide (CO<sub>2</sub>) is one of the most abundant solid components in icy grain mantles within molecular clouds. Recent astronomical observations by the Spitzer Space Telescope have revealed that the column density of solid CO<sub>2</sub> is high and almost constant relative to H<sub>2</sub>O.<sup>19,20</sup> It has been demonstrated theoretically that gas-phase reactions are unsuitable for the formation of the abundant CO<sub>2</sub> typically observed<sup>2</sup> and

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experimentally that abundant CO<sub>2</sub> can be formed by energetic irradiation, such as by UV or ions, of pure solid CO, H<sub>2</sub>O/CO binary ices, and other astrophysically relevant ices containing CO.<sup>21–24</sup> We recently reported that solid CO<sub>2</sub> can be formed by nonenergetic (*i.e.*, without external energetic sources such as photons and ions) surface reactions between CO and OH radicals at 10 and 20 K.<sup>8</sup> More recently, CO<sub>2</sub> formation through the same reaction (CO + OH) was reported by other groups.<sup>25,26</sup> These findings indicate that CO<sub>2</sub> formation can occur inside dense molecular clouds, where the UV field is relatively weak, which is in agreement with astronomical observations.<sup>20,27,28</sup> However, it remains unknown whether nonenergetic reactions yield CO<sub>2</sub> at higher temperatures.

In the present paper, we discuss the formation routes of H<sub>2</sub>O and other molecules (*e.g.*, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) that form on an aluminum (Al) substrate when neutral species in H<sub>2</sub>O discharge plasma (H, O, OH, H<sub>2</sub>, and O<sub>2</sub>) are deposited at 40–60 K. At these temperatures, H<sub>2</sub>O formation via H-related reactions (*e.g.*, hydrogenation to O and O<sub>2</sub>) is expected to occur less frequently because of very short residence time of H atom at the surface, which means that OH-related routes of H<sub>2</sub>O formation are better studied in the present experiment. This is the first report to investigate H<sub>2</sub>O formation pathway through surface reactions of two OH radicals (OH + OH) at low temperatures. We also performed experiments on the co-deposition of plasma-derived neutral species with CO at the same temperatures, to show the efficiency of CO<sub>2</sub> formation at up to 60 K.

## 2 Experimental settings

Experiments were performed using the Apparatus for Surface Reaction in Astrophysics (ASURA) system. Details of this apparatus and experimental conditions have been described previously.<sup>8,9,29</sup> Briefly, OH radicals, together with H atoms, were produced in an H<sub>2</sub>O microwave-discharge plasma<sup>30</sup> in a Pyrex tube. H<sub>2</sub>O dissociation may also lead to the direct formation of H<sub>2</sub> and O. These species are denoted as H<sub>2</sub>O fragments in this paper. H<sub>2</sub>O fragments were transferred via a series of poly(tetrafluoroethylene) and Al tubes, cooled to 100 K in the Al tube which was connected to another He refrigerator, and impinged on the substrate. The OH radicals are thought to be excited when formed in plasma, but after many collisions with the cold aluminum pipe, they are thermalized to 100 K and should already be vibrationally and electronically in the ground state, as expected in the gas-phase collision,<sup>31</sup> before reacting on the cold substrate (40–60 K). The deposition rate of OH radicals could not be measured directly, but can be roughly estimated from the rates of H<sub>2</sub>O<sub>2</sub> formation and H<sub>2</sub>O deposition when the microwave source is turned off,<sup>8,9</sup> yielding a value of approximately  $1.2 \times 10^{13}$  radicals cm<sup>-2</sup> s<sup>-1</sup>. CO molecules were co-deposited with the H<sub>2</sub>O

fragments onto the Al substrate for 120 min. The deposition rate of CO molecules was  $1.4 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. The reaction products were monitored in situ by infrared (IR) reflection-absorption spectroscopy with a resolution of 4 cm<sup>-1</sup> in the spectral range between 4000 and 700 cm<sup>-1</sup>. The desorbed species from the substrate were monitored using a quadrupole mass spectrometer (QMS). A temperature for each experiment was chosen between 40 and 60 K, and the temperature of the Al substrate was maintained at that temperature throughout the experiment.

## 3 Results and Discussion

### 3.1 Deposition of H<sub>2</sub>O fragments

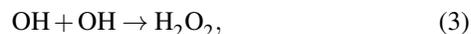
When the H<sub>2</sub>O fragments were solely deposited onto the Al substrate at 40 K, we observed the formation of H<sub>2</sub>O<sub>2</sub> ( $\sim 3300$ , 2849, and 1410 cm<sup>-1</sup>), H<sub>2</sub>O ( $\sim 3300$  and 1645 cm<sup>-1</sup>), and O<sub>3</sub> (1040 cm<sup>-1</sup>) in the IR spectrum of the reaction product (see Fig. 1; hereafter, this experiment is denoted as the blank experiment). Detailed assignments of these molecules have been reported elsewhere.<sup>32–34</sup> The formation of these molecules was also observed at 50 K, but not at 60 K (data not shown). Because their desorption temperatures are higher than 60 K, we conclude that H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub> were not formed in the gas phase but on the Al substrate. Trace amounts of CO<sub>2</sub> were observed in the spectrum, but CO<sub>2</sub> was not a reaction product, as explained previously.<sup>8,9</sup>

QMS analyses revealed that molecular oxygen (O<sub>2</sub>) was formed when the microwave source was turned on. However, we cannot deduce whether O<sub>2</sub> was formed on the Al surface or in the radical source. Brunet et al.<sup>35</sup> proposed that O<sub>2</sub> is formed on the inner wall of the radical source when H<sub>2</sub>O is dissociated in microwave-induced plasma. Nevertheless, we believe that O<sub>2</sub> was partly formed by the following surface reactions:



Given that atomic O is present on the Al surface, these two reactions are expected to occur. The presence of atomic O is supported by the formation of O<sub>3</sub>, as explained below.

For H<sub>2</sub>O<sub>2</sub> formation, we considered the occurrence of the following reactions under the present experimental conditions:



Reaction (3) may be the predominant route of H<sub>2</sub>O<sub>2</sub> formation, because it has no activation barrier.<sup>36</sup> It has been demonstrated experimentally that reactions (4) and (5) have essentially no barriers<sup>13</sup> and are effective at yielding H<sub>2</sub>O<sub>2</sub>, even at

40 K;<sup>37</sup> hydrogenation of O<sub>2</sub> is likely to contribute to H<sub>2</sub>O<sub>2</sub> formation. However, when O<sub>2</sub> was co-deposited with H<sub>2</sub>O fragments onto the Al substrate at 10 K, the column density of the subsequently formed H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> was almost the same as that in the blank experiment at the same temperature. This finding indicates that reactions (4) and (5) are very minor at 10 K and should also be at 40 K. Therefore, we assume that very little atomic H is contained in the H<sub>2</sub>O fragments, a large fraction of atomic H is released into the gas phase prior to any reaction, and/or most of the atomic H reacted with itself to form H<sub>2</sub> on the surface.

Cuppen et al.<sup>17</sup> proposed another H<sub>2</sub>O<sub>2</sub> formation pathway from HO<sub>2</sub>:



They also proposed that HO<sub>2</sub> radicals can dissociate into H + O<sub>2</sub> in low-temperature ices without energy inputs:



However, these reactions are not expected to occur under the present experimental conditions because reactions (6) and (7) are highly endothermic, with large barriers of 13100 and 24000 K, respectively.<sup>36</sup>

The following are possible routes of H<sub>2</sub>O formation:<sup>18,38</sup>

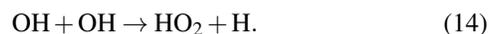
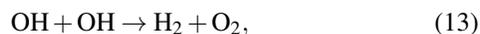


Reactions (8)–(10) have no barriers, while reactions (11) and (12) have barriers of ~2000 K<sup>39</sup> and ~2100 K,<sup>38</sup> respectively. At lower temperatures (~10 K), barrierless reactions related to atomic H—reactions (8) and (9)—are effective because of the sufficiently long residence time of atomic H.<sup>12,17</sup> Reaction (11) can also occur because of a tunneling effect.<sup>13</sup> Reaction (12) has yet to be investigated experimentally but is expected to occur at temperatures as low as 10 K through quantum tunneling.<sup>40</sup> Under the present experimental conditions, however, reactions related to atomic H—reactions (8), (9), and (11)—are not expected to occur as mentioned earlier. Moreover, the residence time of H<sub>2</sub> on the Al substrate at 40 K would be too short for reaction (12) to occur through quantum tunneling.<sup>41</sup> Therefore, the predominant route leading to H<sub>2</sub>O formation is most likely reaction (10) in this experiment.

In addition to H<sub>2</sub>O formation pathways, one may assume that the observed H<sub>2</sub>O includes nondissociated H<sub>2</sub>O from the radical source. However, little H<sub>2</sub>O was observed in the blank experiment at 60 K (data not shown). We assume that dissociation fraction of H<sub>2</sub>O is near unity and/or most H<sub>2</sub>O from the

source was adsorbed on the inner wall of the aluminum pipe, which was cooled to 100 K.

We proposed above that reactions of two OH radicals (OH + OH) are solely responsible for the formation of both H<sub>2</sub>O via reaction (10) and H<sub>2</sub>O<sub>2</sub> via reaction (3). In addition, the following reactions have been studied in the gas phase:<sup>42</sup>



However, reactions (13) and (14) are not expected to occur under the present experimental conditions, because these routes have large barriers of more than 25000 K.<sup>42</sup>

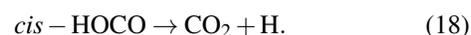
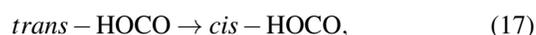
Next, we calculated the column densities of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> that formed in the blank experiment at 40 K, using the band strengths for the peaks at 1645 and 1410 cm<sup>-1</sup>, respectively.<sup>13</sup> The column density of H<sub>2</sub>O<sub>2</sub> was four times higher than that of H<sub>2</sub>O, indicating that the branching ratios for the formation of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> by OH + OH were 0.2 and 0.8 at 40 K, respectively. At 50 K, on the other hand, we could not calculate these column densities because of the low signal-to-noise ratio of the IR spectrum.

The formation pathway of O<sub>3</sub> is much simpler than that of other molecules, and is limited to the following reaction:<sup>4</sup>



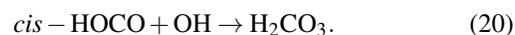
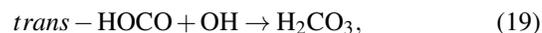
### 3.2 Codeposition of H<sub>2</sub>O fragments with CO

When H<sub>2</sub>O fragments were codeposited with CO at 40 K, we observed an increase in the CO<sub>2</sub> peak intensity at 2353 cm<sup>-1</sup> compared with the blank experiment (Fig. 1). It has been proposed that CO<sub>2</sub> forms by the following reaction routes under the present experimental conditions:<sup>8</sup>



Neither *trans*- nor *cis*-HOCO radicals were identified in the reaction products at 40–60 K, probably because HOCO radicals are highly reactive at these temperatures.<sup>8,43</sup> Other routes to the formation of CO<sub>2</sub> such as CO + O or HOCO + H are unlikely to occur under the present experimental conditions as already mentioned in our previous study.<sup>8</sup>

In addition to CO<sub>2</sub>, new peaks appeared at around 1750, 1500, and 1300 cm<sup>-1</sup>, which were derived from carbonic acid (H<sub>2</sub>CO<sub>3</sub>) formed via the following reactions:<sup>9</sup>



Further results and discussion of the formation of H<sub>2</sub>CO<sub>3</sub> have been published elsewhere.<sup>9</sup> The formation of HCO, H<sub>2</sub>CO,

CH<sub>3</sub>OH, and HCOOH was not positively identified in the IR spectra of the reaction products, indicating that the hydrogenation of CO and HOCO did not occur under the present experimental conditions.

Note that with increasing substrate temperature, the formation of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub> becomes less effective, while CO<sub>2</sub> formed even at 60 K (Fig. 2). H<sub>2</sub>CO<sub>3</sub> formed at 50 K, but negligible amounts were produced at 60 K (Fig. 2a). These results imply that once HOCO radicals are formed, they can reside on the surface, even at 50 K, and further yield CO<sub>2</sub> + H or react with additional OH radicals to yield H<sub>2</sub>CO<sub>3</sub>. At 60 K, the HOCO radicals may rapidly yield CO<sub>2</sub> through reactions (16)–(18). Fig. 2a shows that little or no H<sub>2</sub>O<sub>2</sub> formation occurred at 60 K, although CO<sub>2</sub> was formed. This result indicates that the actual deposition rate of OH radicals could be lower than the estimated value ( $1.2 \times 10^{13}$  radicals cm<sup>-2</sup> s<sup>-1</sup>) and hence the actual one is much lower than that of CO ( $1.4 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup>); OH has little chance to react with another OH before desorbing from the Al substrate. Nevertheless, our results clearly indicate that formation of CO<sub>2</sub> quickly occurred before CO and OH desorb from the Al substrate in spite of their very short residence time on the substrate at 60 K.

The peak position and shape of the CO<sub>2</sub> asymmetric stretch varied with substrate temperature (Fig. 2b). At 40 K, a strong peak appeared at 2353 cm<sup>-1</sup>, while at 50 K, the peak appeared at 2363 cm<sup>-1</sup>, concurrent with the appearance of a small shoulder at 2377 cm<sup>-1</sup>. At 60 K, a strong peak appeared at 2380 cm<sup>-1</sup>, with two small shoulders at 2345 and 2362 cm<sup>-1</sup>. It has been reported that the asymmetric-stretch mode of pure, solid CO<sub>2</sub> falls at 2344 cm<sup>-1</sup> at 10 K, and its position changes little during warming up to 80 K.<sup>44</sup> These findings are clearly inconsistent with our experimental results. Therefore, a different explanation is required for the temperature dependence of the peak positions and shapes in Fig. 2b. Previous studies have revealed that the peak positions for the asymmetric mode of CO<sub>2</sub> crystals vary with size and conformation.<sup>45–48</sup> For CO<sub>2</sub> crystals, their so-called transverse optical and longitudinal optical modes fall at 2344 and 2381 cm<sup>-1</sup>, respectively,<sup>47</sup> which is consistent with the peak positions of CO<sub>2</sub> formed at 60 K (Fig. 2b). We assume that the band-shifting and splitting feature seen at higher temperatures is related to the degree of crystallinity and conformation of CO<sub>2</sub> formed at each temperatures. At 50 and 60 K, the CO<sub>2</sub> peak shape and position could also be perturbed by co-existing H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, or H<sub>2</sub>CO<sub>3</sub> on the Al substrate. In view of molecular-vibrational spectroscopy, it may be of value to investigate the properties of the crystalline CO<sub>2</sub> formed in the present study; however, this is beyond the scope of our study.

The column density of CO<sub>2</sub> increased linearly with experimental time at each temperature (Fig. 3). The band strength for CO<sub>2</sub> ( $7.6 \times 10^{-17}$  cm molecules<sup>-1</sup>) was derived from Ger-

akines et al.<sup>32</sup> The variation in CO<sub>2</sub> column density with time is clearly different from that in the same experiment at lower temperatures (10 and 20 K), where the column density reaches saturation with time.<sup>8</sup> We reported previously that as the reaction proceeds, there is an increasing number of surface sites where CO and OH can be adsorbed, resulting in a decrease in the frequency of these species encountering each other on the surface at 10 and 20 K.<sup>8</sup> In addition, the mobility of CO and OH show an increase with increasing temperature. In this case, the surface morphology constrains the reaction frequency to a much smaller extent, although the residence time on the surface should decrease for both species. Consequently, the CO<sub>2</sub> column density showed a linear increase with time (Fig. 3).

CO<sub>2</sub> formation becomes less effective with increasing temperature (Fig. 3). The conversion factor of CO into CO<sub>2</sub> was calculated to be 1.4%, 0.8%, and 0.3% at 40, 50, and 60 K, respectively. This temperature dependence is explained by the shorter residence times of CO and OH on the surface at higher temperatures. Although the conversion factor is not large compared with that for the same reaction at 10 K (which yielded values up to 10%),<sup>8</sup> the present results are of use because, to the best of our knowledge, this is the first experimental confirmation of the formation of solid CO<sub>2</sub> at temperatures as high as 60 K.

## 4 Summary

We investigated the reactions of H<sub>2</sub>O fragments (H, O, OH, H<sub>2</sub>, and O<sub>2</sub>) on an Al substrate at 40–60 K, revealing that the formation of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and O<sub>3</sub> occurred on the substrate and not in the gas phase. We propose that the predominant formation route of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O was a reaction between two OH radicals, where the branching ratios of the products were 0.8 for H<sub>2</sub>O<sub>2</sub> and 0.2 for H<sub>2</sub>O. The present study is the first to show experimentally that reactions of two OH radicals can yield H<sub>2</sub>O under astrophysically relevant conditions.

When CO and H<sub>2</sub>O fragments were co-deposited onto the Al substrate, CO<sub>2</sub> was formed by surface reactions of CO with nonenergetic OH radicals that formed in H<sub>2</sub>O discharge plasma, even at 60 K. The conversion factor of CO to CO<sub>2</sub> was up to 1.4% under the present experimental conditions. H<sub>2</sub>CO<sub>3</sub> formation was observed at 40 and 50 K, but was negligible at 60 K. HOCO radicals were not identified in IR spectra of the reaction products, unlike for the same experiment at 10 K.<sup>8</sup> However, the formation of CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> indicates that HOCO radicals were actually formed at 40–60 K, although they would have been rapidly consumed by further reactions to yield these molecules. These results may suggest that CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> form via nonenergetic processes in relatively warm environments such as protostars.

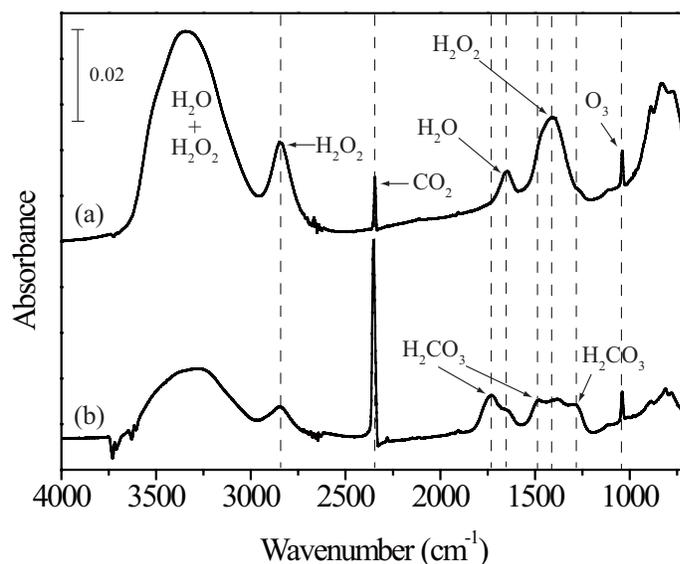
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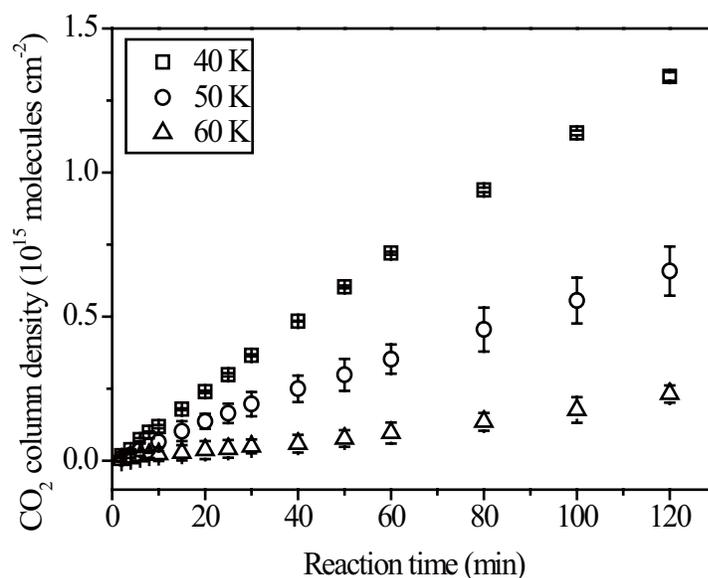
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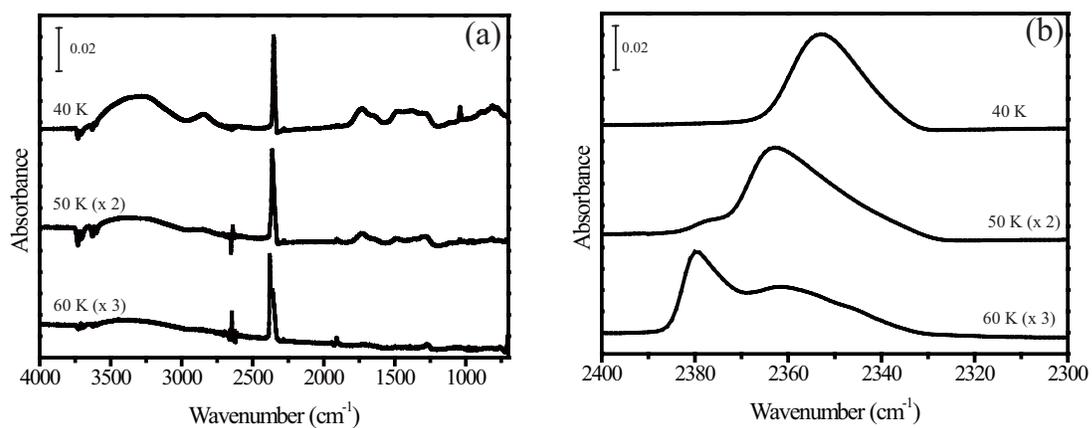
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**Fig. 1** FTIR spectra obtained after (a) deposition of the H<sub>2</sub>O fragments and (b) codeposition of the H<sub>2</sub>O fragments with CO at 40 K. Vertical lines are provided for guidance.



**Fig. 3** Variations in CO<sub>2</sub> column density with experimental time at 40, 50, and 60 K.



**Fig. 2** FTIR spectra obtained after codeposition of the H<sub>2</sub>O fragments with CO: (a) 4000–700 cm<sup>-1</sup> and (b) 2400–2300 cm<sup>-1</sup>. From top to the bottom: 40, 50, and 60 K. For peak assignments, refer to Fig. 1.