

# Spectroscopy and Processing of Interstellar Ice Analogs

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**Abstract.** Recent results from the Raymond and Beverly Sackler Laboratory for Astrophysics on spectroscopy and processing of interstellar ice analogues are summarized. This includes thermal desorption studies of pure, layered and mixed CO, N<sub>2</sub> and O<sub>2</sub> ices, and infrared spectroscopy and heating of CO-CO<sub>2</sub>, CO-H<sub>2</sub>O, CO-HCOOH, CO-CH<sub>4</sub> and CO-CH<sub>3</sub>OH layered and mixed ices. Laboratory data of CO-surface adsorbates show good agreement with the unidentified 2175 cm<sup>-1</sup> interstellar feature. Complementary ab initio quantum chemical calculations and molecular dynamics simulations have been performed to provide insight into the gas-grain interactions and interstellar ice processing. This includes the first molecular dynamics study of the photodissociation of water ice and the corresponding photodesorption efficiencies. The relevance of these data in the analysis of astronomical data is emphasized throughout.

**Keywords:** Laboratory astrophysics; interstellar ices, solid-state spectroscopy, molecular dynamics

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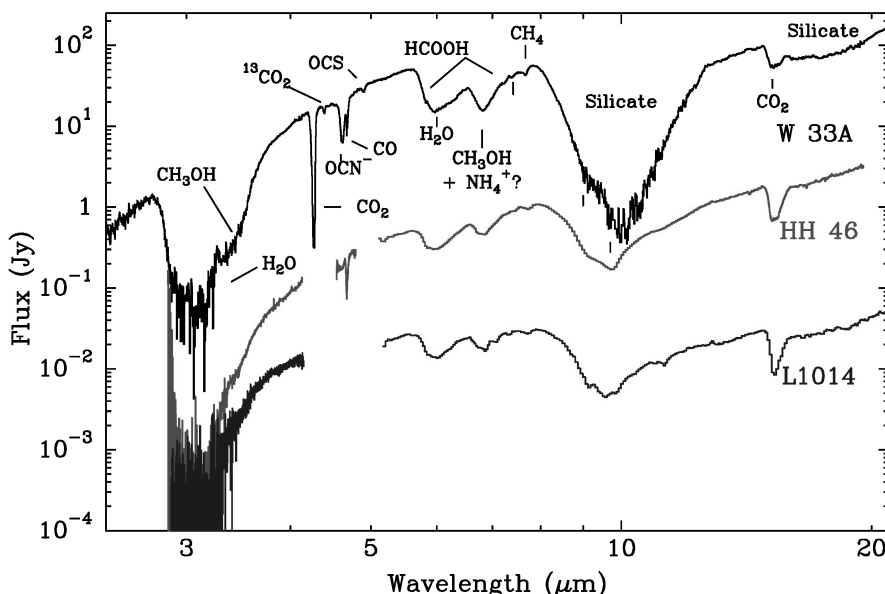
## INTRODUCTION

The gas and dust in interstellar clouds form the raw material from which future planetary systems are built. The study of the production of molecules in space and their incorporation into new solar systems thus provides insight into the pre-biotic evolution of our own planetary system. Much progress has been made in recent years in unraveling the physical structure of protostellar and protoplanetary regions through a combination of infrared and (sub-)millimeter observations. However, much of this scenario is based on imaging data. Only spectroscopic observations can provide constraints on the chemical composition of the gas and dust during the star- and planet formation process. Because the chemical abundances respond to changes in the physical conditions (e.g., temperature, UV radiation), the molecules also serve as key probes of physical parameters and evolutionary state [1].

Experiments in the Raymond and Beverly Sackler Laboratory at Leiden traditionally focus on interstellar ices, but have more recently expanded to include gas-phase spectroscopy and processes [e.g., 2,3]. They are driven by modern observations. In particular, the Infrared Space Observatory (ISO), which flew from 1995-1998, provided the first complete database of infrared spectra of protostars unhindered by the Earth's atmosphere (Figure 1). Ices are a dominant solid component in star-forming regions, with abundances of solid H<sub>2</sub>O and CO that are comparable to those of gas-phase CO, the second most abundant interstellar molecule. A full inventory of the different ice components has been made for the first time, thanks to the ISO data coupled with laboratory experiments [4,5]. Moreover, the high-quality data have allowed evolutionary trends to be discovered since both the ice structure and the condensation/evaporation of ices are very sensitive functions of the thermal history of the region [6,7].

The ISO data were limited to high-mass protostars ( $>10^3 L_{\text{Sun}}$ ). New ground-based instrumentation on 8-m class telescopes such as the ESO Very Large Telescope (VLT) and the Keck Observatory, together with the Spitzer Space Telescope, allow protostars with luminosities as low as 10% of that of our Sun to be observed. Figure 1 includes recent results on the HH 46 solar-mass protostar and the L1014 substellar object [8]. Very strong ice absorptions are found which at first resemble those seen toward the much more luminous W 33A massive protostar.

Weaker features such as those due to solid  $\text{CH}_4$ ,  $\text{HCOOH}$  and  $\text{NH}_3$  are detected as well for the first time toward low-mass sources. However, on closer inspection subtle differences are found, both between low- and high-mass protostars and within one category. For example, the solid  $\text{CO}_2$  abundance is up to a factor of 2 higher in low-mass sources. Species like  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$  and  $\text{OCN}^-$  show more than an order of magnitude variation between low-mass sources, even on scales as small as 1000 AU [9,10,11]. Spitzer also has the sensitivity to observe background stars behind quiescent molecular clouds, providing constraints on the ice composition prior to star formation [12]. These solid-state data are complemented by observations of gas-phase molecules using submillimeter telescopes such as the James Clerk Maxwell Telescope (JCMT). In particular, in the ‘hot cores’ ( $T > 100$  K) near protostars, the ices evaporate back into the gas phase, where they can initiate a more rapid gas-phase chemistry leading to even more complex organic species. Thus, such data provide indirect information on the ice composition, at a level which can be orders of magnitude more sensitive than the direct infrared data. Identification of the solid-state profiles and understanding the chemical processes associated with ice formation and evolution are major goals of the research in the Sackler Laboratory. We summarize here results from our laboratory over the last few years.



**FIGURE 1.** Top: ISO infrared spectrum toward the deeply embedded massive protostar W-33A ( $10^5 L_{\text{Sun}}$ ), showing many strong absorption features due to interstellar ices [13]. Middle and bottom: Combined VLT/Keck (3-5  $\mu\text{m}$ ) and Spitzer (5-20  $\mu\text{m}$ ) spectra of the solar mass protostar HH 46 ( $20 L_{\text{Sun}}$ ) and the substellar object L1014 ( $0.1 L_{\text{Sun}}$ ) [8]. The ground-based spectra have a spectral resolving powers  $R = 10^3$ - $10^4$  whereas the Spitzer spectra have  $R \sim 100$  (5-10  $\mu\text{m}$ ) and  $R = 600$  ( $> 10 \mu\text{m}$ ). Thus the solid state features in the 5-10  $\mu\text{m}$  range are not fully resolved. The tickmarks at 9.0 and 9.7  $\mu\text{m}$  indicate the positions of features of solid  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$ , respectively.

## EXPERIMENTAL METHODS

The equipment for studies of interstellar ices in the Sackler laboratory consists of three set-ups – CRYOPAD, SURFRESIDE and the traditional HV-SETUP. Most of the results reported here have been obtained with the CRYOPAD ultra-high vacuum (UHV) and the traditional high-vacuum (HV) set-up [14]. The goal of SURFRESIDE (SURFace REAction SIMulation DEvice) is to study atom-molecule reactions on surfaces at interstellar temperatures [15]. A fourth solid-state experiment, CESSS (Cavity Enhanced Solid-State Spectrometer) is being built to perform optical spectroscopy of ices following UV bombardment.

The CRYOgenic Photoproduct Analysis Device (CRYOPAD) is specifically designed to study the formation and desorption of volatile complex organic molecules as expected in ‘hot cores’ near protostars by heating and/or by irradiation of ices with intense VUV irradiation. Ultra-high vacuum conditions ( $5 \times 10^{-11}$  mbar) are routinely achieved and sensitive detection techniques such as TPD (temperature programmed desorption) and RAIRS (reflection absorption infrared spectroscopy) are used to characterize interstellar ice analogues. The ices are grown at 14 K on a

gold surface with mono-layer precision and the spectroscopic and thermal properties of pure, layered and mixed ices can be studied. More details can be found in [16,17].

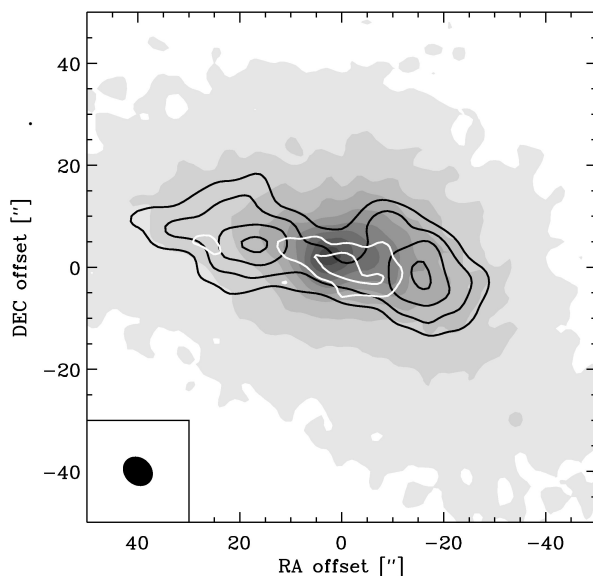
Recent VLT-ISAAC observations suggest that more than 60% of CO ice is present in its pure form, probably in a layer segregated from other ice species [18]. Typical ice thicknesses are thought to be of order 40 L, where 1 L=1 Langmuir =  $1 \times 10^{-6}$  Torr s<sup>-1</sup>, which roughly corresponds to 1 monolayer per unit area (1cm<sup>2</sup>) of material on the surface. Thus, ice mixtures and ice layers are both astrophysically relevant.

## THERMAL DESORPTION AND STICKING

### Astronomical Motivation

In the cold pre-stellar cores prior to star formation, the temperatures are very low (<10 K) and the densities high (>10<sup>5</sup> cm<sup>-3</sup>) so that most molecules collide with the grains and stick in timescales of less than 10<sup>5</sup> yr, less than the age of the core. This freeze-out is clearly observed in several cores with central condensations such as B68 [19], where millimeter observations show that CO is nearly absent from the dense gas. Surprisingly, however, N<sub>2</sub>H<sup>+</sup> (as tracer of the unobservable N<sub>2</sub>) is still detected in regions of heavy freeze-out and disappears only at the highest densities and lowest temperatures. This anticorrelation between N<sub>2</sub>H<sup>+</sup> and CO is also beautifully seen in protostellar regions, where N<sub>2</sub>H<sup>+</sup> is prominent in the outer envelopes where CO is frozen out (see Figure 2) [20]. One explanation for this anticorrelation is that the binding energy of N<sub>2</sub> to the ice is less than that of CO, with the ratio between the two binding energies typically taken to be ~0.65. Another effect is the ion-molecule chemistry itself: CO is the main destroyer of N<sub>2</sub>H<sup>+</sup>, so its abundance increases when CO is removed from the gas.

N<sub>2</sub> and O<sub>2</sub> are predicted to be the main reservoir of nitrogen and oxygen deep inside molecular clouds. In contrast with N<sub>2</sub>, O<sub>2</sub> cannot readily be probed by a trace ion. Deep searches for O<sub>2</sub> in dark clouds have revealed only upper limits, with abundances below 10<sup>-6</sup> with respect to H<sub>2</sub> [21]. Some of the missing O<sub>2</sub> could be in solid form on grain surfaces and be released in the gas only at higher temperatures.



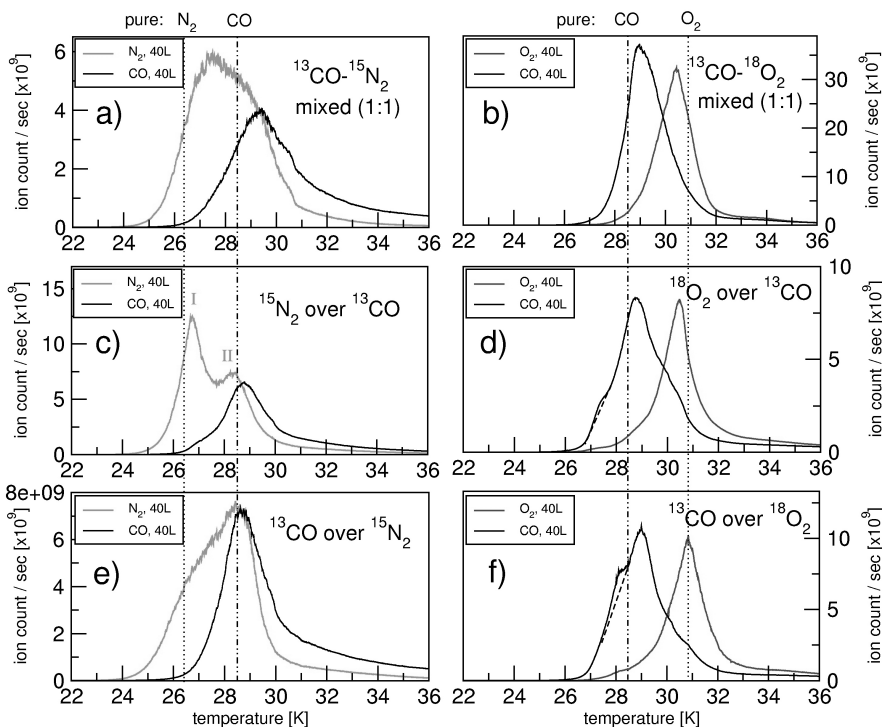
**FIGURE 2.** Interferometer image of the protostellar core L483 ( $d=200$  pc,  $10''=2000$  AU, with 1 AU=distance Sun-Earth) obtained with the Owens Valley Radio Observatory. The grey-scale indicates the continuum radiation from cold dust at  $\sim 30$  K. The black thick line delineates the N<sub>2</sub>H<sup>+</sup> emission, which is prominent in the outer cold envelope where CO, indicated by the white contours, is frozen out. In the inner warm envelope above 30 K close to the protostars, CO evaporates back into the gas phase. [20].

## CO-N<sub>2</sub>

In order to investigate the absolute and differential desorption behavior of CO and N<sub>2</sub>, CRYOPAD experiments on pure, layered and mixed ices of CO and N<sub>2</sub> have been performed for astrophysically relevant ice thicknesses by [22,23]. The results presented in Figure 3 clearly show that N<sub>2</sub> does desorb prior to CO in all ice samples, but that the ratio between the binding energies is only 0.9-1, depending whether pure, mixed or layered samples are studied. For pure CO and N<sub>2</sub>, binding energies of  $855 \pm 25$  K and  $790 \pm 25$  K are found, respectively. Thus, binding energy ratios as low as 0.65 are not supported by the experimental data. In mixed (CO:N<sub>2</sub>=1:1) and layered (CO above or below N<sub>2</sub>) ice systems, both molecules become mobile within the ice matrix at temperatures as low as 20 K and mix. Consequently, at least half of the N<sub>2</sub> does not leave the surface until CO evaporates and astrochemical models need to include a stepwise desorption of ices. A detailed model of the experimental data to provide binding energies and order of the kinetics to be used in astrochemical models has been presented in [23].

## CO-O<sub>2</sub>

Similar CRYOPAD studies have been performed on CO-O<sub>2</sub> ices [17,24]. In contrast with N<sub>2</sub>, O<sub>2</sub> desorbs at somewhat higher temperatures than CO, irrespective of whether it is in pure, layered or mixed ices. Thus, O<sub>2</sub> interacts only weakly with CO, either due to the weak quadrupole interaction of O<sub>2</sub> with CO compared with N<sub>2</sub>-CO or because O<sub>2</sub> has a different crystalline structure than CO at low temperatures, or both. CO is observed to undergo microcrystallization in the 20-27 K range, as reflected in the sensitive CO RAIR spectra.



**FIGURE 3.** TPD spectra of mixed and layered <sup>13</sup>CO, <sup>15</sup>N<sub>2</sub> and <sup>18</sup>O<sub>2</sub> ices. a. Equimolar mixed CO:N<sub>2</sub> (1:1) ices of 80 L thickness; b. Equimolar mixed CO:O<sub>2</sub> (1:1) ices; c. Layered structure of N<sub>2</sub> over CO. d. Layered structure of O<sub>2</sub> over CO. e. Layered structure of CO over N<sub>2</sub>; f. Layered structure of CO over O<sub>2</sub>. The dashed lines indicate the peak positions of pure N<sub>2</sub>, CO and O<sub>2</sub> for 40 L thickness. Figure based on [17].

## Sticking Probabilities

Our experimental setup does not allow a direct determination of the sticking coefficients  $S$  with the accuracies that can be achieved by molecular beam experiments. However, lower limits on the uptake coefficient can be obtained by comparing the gas load of species reaching the mass spectrometer during the deposition time and the gas load at room temperatures monitored over the same period of time during deposition. For all species and combinations studied here, these lower limits range from 0.85 to 0.95 at 14 K. Thus, it is likely that they are all very close to unity at 10 K. Models which use sticking probabilities as low as 0.1 [25] are not supported by these data.

To gain more insight into the sticking process, classical trajectory calculations have been performed on the adsorption of thermal CO to the surfaces of amorphous and crystalline water ice for a range of energies [26]. For hyperthermal CO, the sticking probability is found to decrease with incidence energy and with the incidence angle. No surface penetration is found to occur even at high energies, but the impinging molecule may damage the surface significantly when it hits in the center of a hexagonal ring of crystalline ice. At low temperatures relevant for interstellar conditions, the calculations predict a high adsorption probability close to unity, consistent with the experimental results.

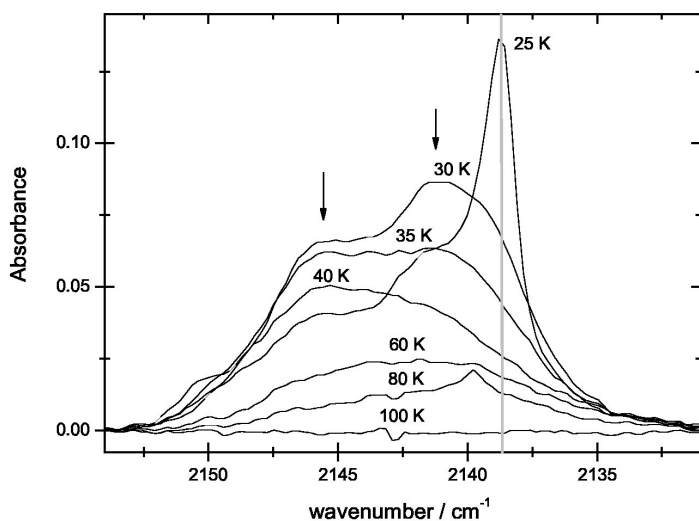
## INFRARED SPECTROSCOPY

### CO-various species

The HV setup was used to study in detail the spectroscopy and desorption behavior of CO in a variety of ice systems, i.e., HCOOH, CO<sub>2</sub>, CH<sub>3</sub>OH, and CH<sub>4</sub>, all of which are found in roughly equal abundances in a variety of high and low mass young stellar objects (see Figure 1) [27,28]. A general comparison of the results shows that CO desorption from layers and mixed ices is significantly different as the temperature of the ice increases. Similarly, the spectroscopy of mixed ices is rather complex whereas that of layered ices looks identical to the pure ices.

### CO-CO<sub>2</sub>

A systematic set of experiments has been performed on the spectroscopic characteristics and thermal desorption of CO and CO<sub>2</sub> in mixed and layered ice configurations [29]. These experiments are triggered by VLT/Keck infrared spectra of solid CO at 4.67  $\mu\text{m}$  [18] and Spitzer data of solid CO<sub>2</sub> at 15  $\mu\text{m}$  [8,30], which show indications of CO-CO<sub>2</sub> mixtures in space. There are two possible scenarios for CO and CO<sub>2</sub> ice to co-exist: either CO condenses from the gas phase prior, or subsequent to, CO<sub>2</sub> surface chemical formation [31], or CO and CO<sub>2</sub> are produced from chemical reactions induced in the ice mantle by irradiative processes. The experiments show that both the spectroscopy and the thermal behavior of CO and CO<sub>2</sub> in mixed and layered ices are significantly different (Figure 4). CO only affects the CO<sub>2</sub> bending mode spectra in mixed ices below 50 K, where it exhibits a single asymmetric band profile in intimate mixtures. In all other ice morphologies the CO<sub>2</sub> bending mode shows a double peaked profile, similar to that observed for pure solid CO<sub>2</sub>. Conversely, CO<sub>2</sub> induces a blue-shift in the peak-position of the CO stretching vibration. As such, the CO<sub>2</sub> bending mode provides clear constraints on the ice morphology below 50 K, whereas beyond this temperature the CO stretching vibration can distinguish between initially mixed and layered ices.

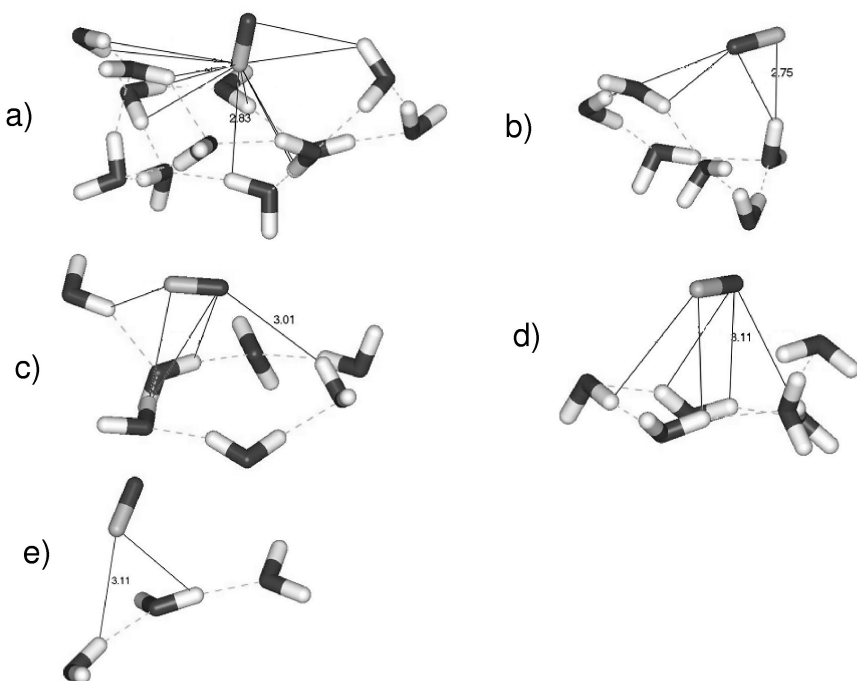


**FIGURE 4.** Thermal evolution of the CO stretching vibration in a 10/1 CO<sub>2</sub>/CO layered ice system from 25-100 K. The thick grey line marks the peak center position of the main spectral feature in pure CO ice. The two arrows indicate the two shoulders that evolve as the temperature increases [29].

### CO-H<sub>2</sub>O and the missing 2152 cm<sup>-1</sup> band

Laboratory data on the CO-H<sub>2</sub>O ice system from the Nottingham laboratory have been used to explain why a 2152 cm<sup>-1</sup> band is never observed in astronomical spectra of CO ice [32]. The 2152 cm<sup>-1</sup> band has been proven by theoretical and laboratory studies to be related to CO molecules bound at dangling OH sites at the surface of an amorphous or crystalline H<sub>2</sub>O ice surface. The fact such bands are missing in space is a key clue to astrochemistry and the location of CO in interstellar ices, as well as the structure of interstellar ice. Careful analysis of laboratory data shows that the water ice must still be porous and amorphous, but that prior to the freeze-out of CO the dangling bond sites must be already occupied - by some molecule which forms stronger hydrogen bonds than CO. Such species could be CO<sub>2</sub>, NH<sub>3</sub> or CH<sub>3</sub>OH.

Quantumchemical calculations of the CO-H<sub>2</sub>O potentials show that the adsorbed CO has an average potential energy of -0.094 eV, but with a large range corresponding to various geometries [33]. In all the adsorbing trajectories in dynamical simulations, CO sits on top of the surface (see Figure 5). Geometry minimizations confirm that the maximum potential energy of adsorbed CO occurs when CO interacts with a dangling OH group, attributed to the secondary (weaker) CO band seen in solid-state infrared laboratory spectra, at 2152 cm<sup>-1</sup>. CO also interacts with bonded OH groups, which are attributed to the primary (stronger) band of solid CO at 2139/2136 cm<sup>-1</sup>. Good agreement with experiments is found, where available.



**FIGURE 5.** Examples of CO-water ice configurations. The  $2152\text{ cm}^{-1}$  feature is associated with the dangling OH as well as with bonded OH, as seen in panels a and b. The  $2139\text{ cm}^{-1}$  feature is associated with CO interacting only with bonded OH, as in panels c, d and e [17].

### CO-surface adsorbates

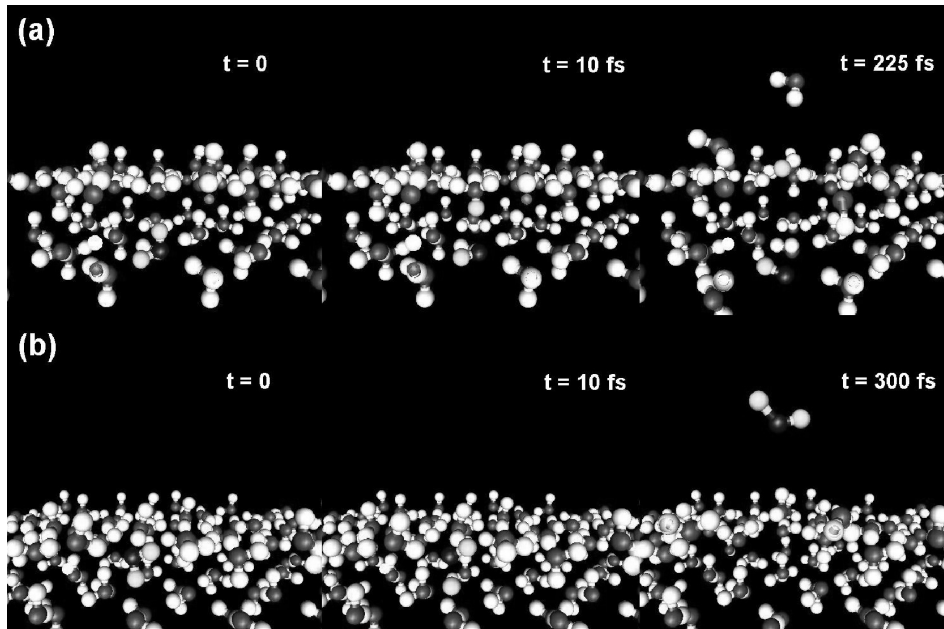
VLT-ISAAC spectra show a new solid-state band at  $2175\text{ cm}^{-1}$  distinctly offset from the  $2164\text{ cm}^{-1}$  OCN<sup>-</sup> feature, which cannot be identified with any known ices [18]. One possible identification is CO directly attached to the silicate surface. The HV setup was used to obtain laboratory spectra of CO chemisorbed to a zeolite surface [34]. Excellent agreement was obtained in all objects where the band was observed. This would constitute the first direct evidence for grain-gas interactions in interstellar and protostellar regions.

### PHOTODESORPTION

Photodesorption of ices plays a role at the edges of molecular clouds and in the upper layers of circumstellar disks, where the ices from the midplane may be mixed up to higher layers and be exposed to copious UV photons from the star. Quantitative photodesorption yields of astrophysically relevant ices are therefore critically important for the outcomes of these models. An experimental study of photodesorption yields has been started in our laboratory, with first results for CO presented in [16].

Complementary to the experiments, theoretical studies of photodesorption of pure water ice have been performed [35,36]. Such calculations provide qualitative and quantitative insight into the dynamics of the photoproducts in the ice. A set of programs has been developed to calculate the photodissociation dynamics of a water molecule in a crystalline and amorphous ice layer at 10 K, using classical molecular dynamics. The final outcome is found to strongly depend on the original position of the photodissociated molecule. For molecules in the first (bi)layer, desorption of H atoms dominates. Deeper into the ice, H atom desorption becomes less important and trapping and recombination of H and OH dominate. The distribution of distances traveled by H atoms in the ice peaks at  $6\text{ \AA}$  with a tail going to  $60\text{ \AA}$ . The mobility of OH radicals is low within the ice with distances of  $\sim 2\text{ \AA}$  except at the surface where OH can move over more than  $80\text{ \AA}$ . Only minor differences are found between amorphous and crystalline ice. Simulated absorption spectra of crystalline ice, amorphous ice, and liquid water are found to be in very good

agreement with experiments. Desorption of H<sub>2</sub>O has a low probability (less than 0.5% yield per absorbed photon) for both types of ice (Figure 6), a prediction which will be tested by future CRYOPAD experiments (see also [37]). In interstellar space the trapped radicals will be available for further reactions in the ice with other species.



**FIGURE 6.** Molecular dynamics simulation of the photodissociation of crystalline ice. In the top figure, the H<sub>2</sub>O is kicked out by the energetic H atom resulting from photodissociation. In the bottom panel, H<sub>2</sub>O from the surface photodesorbs. Figure based on [36].

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## REFERENCES

1. E.F. van Dishoeck and G.A. Blake, *Ann. Rev. Astron. Astrophys.* **36**, 317 (1998).
2. O. Asvany, P. Kumar, B. Redlich, I. Hegemann, S. Schlemmer, and D. Marx, *Science* **309**, 1219, (2005).
3. H. Verbraak, J.N.P. van Stralen, J., Bouwman, J.S. de Klerk, D., Verdes, H., Linnartz, F.M., Bickelhaupt, J. *Chem. Phys.* **123**, 144305 (2005).
4. P. Ehrenfreund and W.A. Schutte, in *Astrochemistry: from Molecular Clouds to Planetary Systems*, IAU Symposium 197, edited by Y.C. Minh and E.F. van Dishoeck (ASP, San Francisco), pp. 135-146.
5. E.L. Gibb, D.C.B. Whittet, A.C.A. Boogert and A.G.G.M. Tielens, *Astrophys. J. Suppl.* **151**, 35 (2004).
6. E.F. van Dishoeck, F.P. Helmich, Th. De Graauw, et al., *Astron. Astrophys.*, **315**, L345 (1996).
7. P. Ehrenfreund, E. Dartois, K. Demyk and L. d'Hendecourt, *Astron. Astrophys.*, **339**, L17 (1998).
8. A.C.A. Boogert, K.M. Pontoppidan, F. Lahuis, et al., *Astrophys. J. Suppl.*, **154**, 359 (2004).
9. K.M. Pontoppidan, C.P. Dullemond, E.F. Van Dishoeck, G.A. Blake, A.C.A. Boogert, N.J. Evans, J.E. Kessler-Silacci and F. Lahuis, *Astrophys. J.*, **622**, 463 (2005).
10. K.M. Pontoppidan, E.F. van Dishoeck and E. Dartois, *Astron. Astrophys.* **426**, 925 (2004).
11. F.A. Van Broekhuizen, K.M. Pontoppidan, H.J. Fraser and E.F. van Dishoeck, *Astron. Astrophys.* **441**, 249 (2005).



12. C. Knez, A.C.A. Boogert, K.M. Pontoppidan, J. Kessler-Silacci, E.F. van Dishoeck, N.J. Evans, J.C. Augereau, G.A. Blake and F. Lahuis, *Astrophys. J.*, **635**, L145 (2005).
13. E.L. Gibb, D.C.B. Whittet, W.A. Schutte, A.C.A. Boogert, J.E. Chiar, P. Ehrenfreund, P.A. Gerakines, J.V. Keane, A.G.G.M. Tielens, E.F. van Dishoeck and O. Kerkhof, *Astrophys. J.* **536**, 347 (2000).
14. P. A. Gerakines, W.A. Schutte, J.M. Greenberg and E.F. Van Dishoeck, *Astron. Astrophys.* **296**, 810 (1995).
15. H.J. Fraser and E.F. van Dishoeck, in ‘Space Life Sciences; Steps toward Origin(s) of Life’ , *Advances in Space research series*, **33**, 14 (2004).
16. F.A. van Broekhuizen, “A Laboratory Route to Interstellar Ice”, PhD thesis, Leiden University, 2005.
17. G.W. Fuchs, K. Acharyya, S.E. Bisschop, K.I. Öberg, F. van Broekhuizen, H.J. Fraser, S. Schlemmer, E.F. van Dishoeck and H. Linnartz, *Faraday Discuss.* **133** (2006) in press,
18. K.M. Pontoppidan, H.J. Fraser, E. Dartois, W.F. Thi, E.F. van Dishoeck, A.C.A. Boogert, L. d’Hendecourt, A.G.G.M. Tielens and S.E. Bisschop, *Astron. Astrophys.* **408**, 981 (2003).
19. E.A. Bergin, J. Alves, T. Huard and C.J. Lada, *Astrophys. J.*, **570**, L101 (2002).
20. J.K. Jørgensen, *Astron. Astrophys.* **424**, 589 (2004).
21. P.F. Goldsmith, G.J. Melnick, E.A. Bergin et al., *Astrophys. J.* **539**, L123 (2000).
22. K.I. Öberg, F. van Broekhuizen, H.J. Fraser, S.E. Bisschop, E.F. van Dishoeck and S. Schlemmer, *Astrophys. J.* **621**, L33 (2005) .
23. S.E. Bisschop, H.J. Fraser, K.I. Öberg, E.F. van Dishoeck, and S. Schlemmer, *Astron. Astrophys.* **449**, 1297 (2006).
24. K. Acharyya, G.W. Fuchs, H.J. Fraser, E.F. van Dishoeck and H. Linnartz, *Astron. Astrophys.* (2006), submitted.
25. D.R. Flower, G. Pineau des Fprets, and C.M. Walmsley, *Astron. Astrophys.* **436**, 933 (2005).
26. A. Al-Halabi, E.F. van Dishoeck and G.J. Kroes, *J. Chem. Phys.* **120**, 3358 (2004).
27. W.Z. Alsindi, D.O. Gardner, E.F. van Dishoeck, E.F. and H.J. Fraser, *Chem. Phys. Lett.* **378** 178, (2003).
28. H.J. Fraser, W.Z. Alsindi, S.E. Bisschop and E.F. van Dishoeck, *Astron. Astrophys.* (2006) to be submitted
29. F.A. Van Broekhuizen, I.M.N. Groot, H.J. Fraser, E.F. van Dishoeck and S. Schlemmer, *Astron. Astrophys.*, **451**, 723 (2006).
30. A.C.A. Boogert, M.R. Hogerheijde and G.A. Blake, *Astrophys. J.* **568**, 761 (2002).
31. K.M. Pontoppidan, *Astron. Astrophys.* (2006) in press.
32. H.J. Fraser, M.P. Collings, J.W. Dever and M.N.R. McCoustra , *MNRAS* **353**, 59 (2004).
33. A. Al-Halabi, H.J. Fraser, G.J. Kroes and E.F. van Dishoeck, *Astron. Astrophys.* **422**, 777 (2004) .
34. H.J. Fraser, S.E. Bisschop, K.M. Pontoppidan, A.G.G.M. Tielens and E.F. van Dishoeck, *MNRAS* **356**, 1283 (2005).
35. S. Andersson, G.J. Kroes and E.F. van Dishoeck, *Chem. Phys. Lett.* **408**, 415 (2005).
36. S. Andersson, A. Al-Halabi, G.J. Kroes and E.F. van Dishoeck, *J. Chem. Phys.* **124**, 64715 (2006).
37. M.S. Westley, R.A. Baragiola, R.E. Johnson and G.A. Baratta, *Nature* **373**, 405 (1995).

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