

# An Experimental Study of the Sublimation of Water Ice and the Release of Trapped Gases

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Received January 27, 1989; revised July 11, 1991

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The sublimation of Ar/H<sub>2</sub>O, CO/H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O mixtures condensed at 23–30 K was investigated. The release of the more volatile component of the ice mixture occurred in several discrete temperature regions. Gas release, as monitored by a mass spectrometer, was correlated with changes in the infrared spectrum of the solid ice. The results are in substantial agreement with those of Bar-Nun and co-workers, who studied ice sublimation using mass spectrometry alone, and Sandford and Allamandola, who used infrared spectroscopy alone. Several different concentrations were used for all gas/H<sub>2</sub>O mixtures, and relative peak intensities during warming were found to depend on the initial gas/H<sub>2</sub>O ratio. The sublimation of H<sub>2</sub>O, CO/H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O ices following irradiation by 1-MeV protons was also studied. Irradiation of CO or CO<sub>2</sub> containing ices resulted in CO<sub>2</sub> or CO release, respectively, in addition to the original species. Some implications for cometary phenomena are given. © 1991 Academic Press, Inc.

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## INTRODUCTION

Understanding how icy mixtures of water and other volatile molecules sublime is a fundamental problem in cometary science. Theoretical models of cometary sublimation have been developed (Delsemme 1982, Mendis *et al.* 1985) and widely used (for example, Whipple 1985, Spinrad 1987, and Stern and Shull 1988). Two common aspects of these models are (i) molecular species will be trapped in the ice of a comet's nucleus until the molecule's characteristic sublimation temperature is reached and (ii) the species will sublime at a continuously increasing rate as the temperature increases until the species is depleted.

As an example of how such descriptions have been used, consider the case of CO. Yamamoto's calculation of its sublimation temperature as 25 K (1985) led Spinrad (1987) to argue from the observation of CO in comet Hal-

ley that "If CO is an abundant parent . . . then we have a strong clue that the main body of comet Halley was not heated to over 25 K during its formative years."

In contrast to these theoretical models of gas trapping and release, are laboratory experiments beginning with Ghormley (1967). His observations of oxygen trapped in amorphous ice showed that when the ice was warmed from 77 K, oxygen was not released continuously, but rather at temperatures around 95, 160, and 214 K. Similar behavior was reported for ices containing argon, nitrogen, and methane. These experiments imply CO can be held in comets far beyond its 25 K sublimation temperature and that its release will be in well-defined temperature regions, in contrast to the prediction of present cometary models.

A more sophisticated version of Ghormley's experiments has been reported by Bar-Nun and co-workers (Bar-Nun *et al.* 1985, 1987, 1988, Bar-Nun and Kleinfeld 1989, Laufer *et al.* 1987, Notesco *et al.* 1991) who used mass spectrometry to study gas releases as gas/H<sub>2</sub>O ices were warmed from ~20 K. In some ices, as many as eight distinct gas releases were observed. Conclusions were drawn about the changes in the solid ice that produced the observed gas-phase results.

Sandford and Allamandola have published a large number of results on gas/H<sub>2</sub>O ices, but focusing on observations of the solid rather than the gas phase (e.g., Allamandola *et al.* 1988, Sandford *et al.* 1988, Sandford and Allamandola 1988, 1990). Infrared (IR) spectra of ices were recorded for many temperatures and gas/H<sub>2</sub>O ratios, and the positions, shapes, widths, and intensities of IR absorptions were studied in detail. Decreases in intensity of IR bands, such as for CO and CO<sub>2</sub>, were used to follow the sublimation of trapped gases. As in the work of

Ghormley (1967) and Bar-Nun *et al.* (1985), gas release occurred in well-defined temperature regions and gas was retained up to sublimation of the H<sub>2</sub>O itself.

An important extension of the previous work on gas trapping and release is to observe *both* the solid and the vapor phases on warming gas/H<sub>2</sub>O ices. For this reason, we have carried out over a hundred experiments on four different ice systems, namely, H<sub>2</sub>O, Ar/H<sub>2</sub>O, CO/H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O. Ices were warmed from 25 to 200 K with gas release being monitored by a mass spectrometer (MS) and changes in the solid phase followed with an IR spectrometer. By combining these two techniques, we have been able to correlate observations of gas release with changes in the solid ice. Finally, we have done some preliminary experiments using 1-MeV proton irradiation to investigate possible effects of cosmic rays on cometary ice sublimation. To our knowledge, only Kouchi (1990) has probed both the solid and the vapor states of cometary ice analogs, using electron diffraction and mass spectrometry. No one has reported results with our combination of IR and mass spectral methods coupled with ionizing radiation.

## EXPERIMENTAL

Experiments began with the preparation of a gaseous mixture at room temperature on a vacuum line and the mixture's deposition on a cold finger at 23–30 K. The deposition rate was 1  $\mu\text{m/hr}$  and the sample thickness was 0.5  $\mu\text{m}$ . The gas/H<sub>2</sub>O ratio in the ice deposit was perhaps somewhat higher than at room temperature in the vacuum line because of H<sub>2</sub>O adsorption in the line. However, the good reproducibility of the results implies that the depletion of H<sub>2</sub>O was minimal.

A grating mid-IR spectrometer (measured wavenumber accuracy about 4  $\text{cm}^{-1}$ , resolution about 2  $\text{cm}^{-1}$ ) served both for following the progress of a deposition and for recording IR reflectance spectra of samples from 200 to 4000  $\text{cm}^{-1}$  (2.5 to 50  $\mu\text{m}$ ). After deposition of an icy sample, its IR spectrum was recorded to check its thickness, using absorption coefficients (Wood and Roux 1982, Kitta and Krätschmer 1983) for  $\bar{\nu} \approx 3200 \text{ cm}^{-1}$ . The ice was then warmed to 200 K, at 3 K/min, and mass spectral measurements were made every 6 sec at preselected  $m/z$  values. A heater epoxied onto the back side of the cold finger allowed the ice sample to be warmed independently of the rest of the cryostat (Moore *et al.* 1988).

Once gas release as a function of temperature had been measured, a second ice sample was prepared for IR study. The spectrum of this ice was recorded at 23–30 K, followed by warming to some specific temperature, such as just past a region of gas release. After 15–20 min the sample was recooled to the original temperature for an-

other IR scan. This warming–recooling cycle was necessary to distinguish permanent spectral changes, caused by irreversible physical changes in the ice, from spectral changes simply due to different temperatures during an IR scan.

Our radiation experiments on H<sub>2</sub>O, CO/H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O ices comprise part of a study of the effects of ionizing radiation (1-MeV protons) on the sublimation of cometary ices. The radiation exposure of each sample was  $\sim 3.1 \times 10^{10}$  protons  $\text{cm}^{-2} \text{ sec}^{-1}$  for 1 hr so that the absorbed dose (absorbed fluence) was essentially the same in all experiments. Experimental constraints prohibited detailed studies of gas sublimation below  $\sim 70$  K in radiation experiments and so we confine our discussion to temperatures above that value. In the future we hope to extend our work to lower temperatures.

Additional experimental details, including drawings of equipment and descriptions of the 1-MeV proton source, have been published in Moore *et al.* (1983, 1988) and references therein. The interested reader should consult those papers for more information than can be provided here.

## RESULTS

### H<sub>2</sub>O Ices

It is well known that a film of amorphous ice is formed when H<sub>2</sub>O is cooled directly from the vapor phase onto a surface with a temperature below about 130 K (Hobbs 1974). As the amorphous ice is warmed it crystallizes, first into a cubic phase beginning around 140 K and then, at a higher temperature, into a hexagonal phase. If the ice is warmed still further it will eventually melt, although the thin films in our experiments completely sublime first.

IR spectra for amorphous and cubic H<sub>2</sub>O ice have been published many times, for example Hardin and Harvey (1973), Bergren *et al.* (1978), Leger *et al.* (1979), Hagen *et al.* (1981, 1982), and Fink and Sill (1982). In the 200–4000  $\text{cm}^{-1}$  mid-IR region, absorptions around 3220, 2200, 1600, and 800  $\text{cm}^{-1}$  all undergo changes in position and shape at the phase transition of amorphous water. However, the mid-IR spectra of the cubic and hexagonal phases of ice are essentially identical (Bertie and Whalley 1964, Bertie and Jacobs 1977).

In our work, we recorded the spectrum of amorphous H<sub>2</sub>O ice immediately after deposition at 23 K and subsequently at 23 K after thermal annealings up to 160 K. No changes in IR absorptions were observed as the sample was warmed to about 40 K and then recooled. Beyond 40 K, gradual small changes occurred that were consistent with the more detailed work of Hagen *et al.* (1981, 1982). The greatest changes in the IR spectrum were at the amorphous-to-cubic phase transition for H<sub>2</sub>O. As our spectra

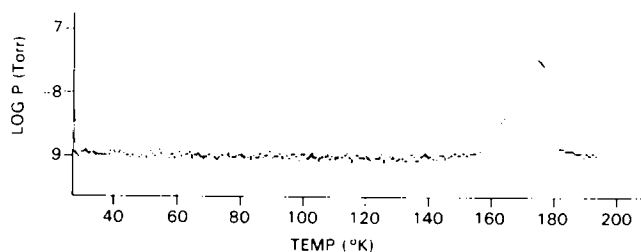


FIG. 1. Sublimation curve for 0.5- $\mu\text{m}$  film of  $\text{H}_2\text{O}$  ice deposited at 30 K.

of amorphous and cubic  $\text{H}_2\text{O}$  are essentially the same as those published by many others (see references above), they are not shown.

We next used a mass spectrometer to record the sublimation curve of a 0.5- $\mu\text{m}$   $\text{H}_2\text{O}$  film and the result is shown in Fig. 1. Apart from the occasional presence of a small peak near 140 K, corresponding to the crystallization of the amorphous ice (Kouchi 1987), this type of curve was observed in all of our experiments involving water. The significant feature is the start of the approximately exponential rise near 155 K. The peak results from the sublimation of the sample film and its gradual disappearance around 175 K.

#### Ar/ $\text{H}_2\text{O}$ Ices

Although argon does not play a significant role in cometary chemistry we investigated Ar/ $\text{H}_2\text{O}$  ices to compare our MS/IR results with the published mass spectral measurements of others (Bar-Nun *et al.* 1985, 1987, Laufer *et al.* 1987). Since argon does not absorb infrared light, IR spectra of deposits with Ar/ $\text{H}_2\text{O}$  ratios of 0.1–0.5 were expected (Ritzhaupt *et al.* 1976), and observed, to be similar to those of pure  $\text{H}_2\text{O}$  ices.

Figure 2 shows sublimation curves for ices with three different Ar/ $\text{H}_2\text{O}$  ratios. The main features are similar to those of Bar-Nun *et al.* (1985, 1987) although our interpretations are slightly different. Argon release is confined to five temperature regions, indicated by I–V in Fig. 2, and most evident in the case of the highest Ar/ $\text{H}_2\text{O}$  ratio. In a few experiments, a sixth region of gas release was seen, a small peak between regions IV and V, perhaps due to the cubic-to-hexagonal phase change for  $\text{H}_2\text{O}$  (Bar-Nun *et al.* 1985, 1987).

IR spectra of ice mixtures with the same concentrations as those in Fig. 2 assisted in the interpretation of each gas release. Warming and recooling the Ar/ $\text{H}_2\text{O}$  ices, in the same manner as with the pure  $\text{H}_2\text{O}$  ices, gave the same changes in the IR absorptions of  $\text{H}_2\text{O}$ , showing no difference due to the presence of argon. IR spectra taken before and after the argon release of region I were essentially

identical, but small changes in the IR bands of  $\text{H}_2\text{O}$  were found before and after warmings through regions II and III. The IR absorptions of  $\text{H}_2\text{O}$  showed the characteristic changes for the amorphous-to-cubic phase transition when Ar/ $\text{H}_2\text{O}$  samples were warmed to region IV and then re-cooled. Finally, all IR peaks disappeared on warming to region V, where mass spectrometry showed that all ices sublimed.

Figure 2 also shows that when argon is released from the amorphous ice in region II, III, and IV, some of the  $\text{H}_2\text{O}$  is carried away as well. This is most easily seen for the highest Ar/ $\text{H}_2\text{O}$  ratio.

The only release of gas that was self-sustaining was in region IV, the amorphous-to-cubic phase change. There, gas release continued even when the ice temperature was held constant. Gas release declined at other temperatures unless the sample was continually warmed.

Figure 2 also shows the general dependence of gas release in each region on the initial gas/ $\text{H}_2\text{O}$  ratio (Bar-Nun *et al.* 1985). As the Ar/ $\text{H}_2\text{O}$  ratio decreases, so does the absolute amount of argon released, as expected. What is

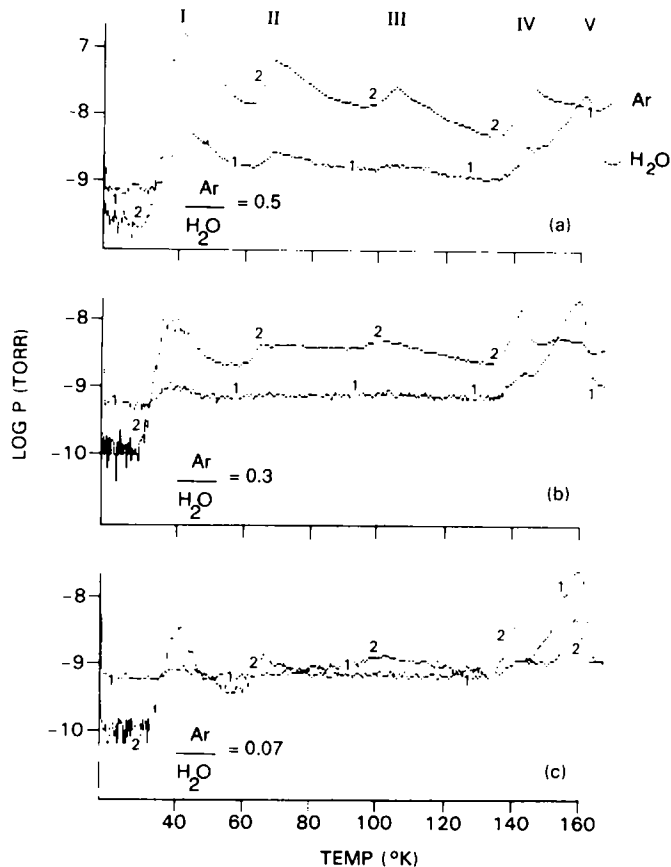


FIG. 2. Sublimation curves for 0.5- $\mu\text{m}$  films of Ar/ $\text{H}_2\text{O}$  ice mixtures deposited at 24 K.

perhaps less expected is the reversal that Fig. 2 shows in the relative amounts of argon released in the two higher temperature regions, IV and V, for samples of equal thickness.

### CO/H<sub>2</sub>O Ices

Since our sublimation curves for CO/H<sub>2</sub>O ices were very similar to those of Fig. 2 for Ar/H<sub>2</sub>O ices, they are not shown here. The same variation of the amount of gas released at different temperatures with the gas/H<sub>2</sub>O ratio of the ice was found. Also similar was the correspondence of the second and third gas releases with small changes in the amorphous H<sub>2</sub>O, as indicated by IR spectroscopy. As with Ar/H<sub>2</sub>O mixtures, CO/H<sub>2</sub>O mixtures showed H<sub>2</sub>O release at even the lowest temperatures for CO sublimation, and CO retention up to the sublimation temperature of the H<sub>2</sub>O itself.

The IR spectra of CO/H<sub>2</sub>O ices contained, in addition to the H<sub>2</sub>O bands, a sharp line near 2140 cm<sup>-1</sup> corresponding to the fundamental vibration of CO. The systematic changes in position and shape of the CO absorption upon varying either the CO/H<sub>2</sub>O ratio or the ice temperature (Sandford *et al.* 1988) were too small to be reliably followed with our spectrometer. However, CO/H<sub>2</sub>O ices did show changes in H<sub>2</sub>O absorptions on warming similar to those seen in pure H<sub>2</sub>O and Ar/H<sub>2</sub>O ices. When a CO/H<sub>2</sub>O sample was warmed to a region of gas release, known from mass spectrometry, IR spectroscopy showed a drop in intensity for the CO absorption.

### CO<sub>2</sub>/H<sub>2</sub>O Ices

Sublimation curves for three CO<sub>2</sub>/H<sub>2</sub>O ices are shown in Fig. 3. Figure 3a for a 3/1 CO<sub>2</sub>/H<sub>2</sub>O ratio is similar to that described, but not shown, by Bar-Nun *et al.* 1985. This ice gave an initial gas release beginning at ~80 K and peaking at 98 K. A second, larger release peaked at 112 K. Reducing the CO<sub>2</sub>/H<sub>2</sub>O ratio to 0.5 and even lower caused substantial changes in the relative amounts of gas released around 146 and 165 K.

CO<sub>2</sub>/H<sub>2</sub>O ices displayed six major IR absorptions, four from H<sub>2</sub>O and two from CO<sub>2</sub>. As in the case of CO, small systematic changes in the IR absorptions of CO<sub>2</sub>, due to variation of the CO<sub>2</sub>/H<sub>2</sub>O ratio or the ice's temperature (Sandford and Allamandola 1990), were not studied. However, with CO<sub>2</sub>/H<sub>2</sub>O ices we did search for, and find, changes in the H<sub>2</sub>O IR absorptions on warming similar to those for pure H<sub>2</sub>O ices. In all experiments, warming a CO<sub>2</sub>/H<sub>2</sub>O sample to a temperature region known, from mass spectrometry, to cause gas release, always reduced the intensity of the two IR bands of CO<sub>2</sub> in the solid.

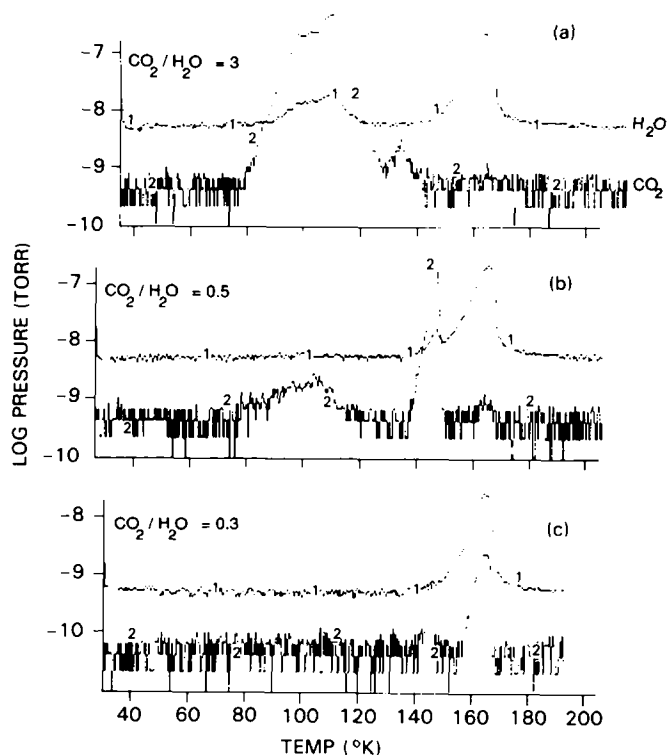


FIG. 3. Sublimation curves for 0.5- $\mu\text{m}$  films of CO<sub>2</sub>/H<sub>2</sub>O ice mixtures deposited at 27 K.

### Radiation Experiments

Because of its presence in all of our experiments, amorphous H<sub>2</sub>O was irradiated and its sublimation curve recorded after the radiolysis to serve as a point of reference. We detected no differences between either the sublimation curves or the IR spectra of irradiated and unirradiated pure H<sub>2</sub>O ice. In particular, the shapes and positions of the four IR bands of amorphous H<sub>2</sub>O were the same before and after the irradiation, indicating that the radiolysis did not cause crystallization of the ice.

It has been known for some time (Moore *et al.* 1983) that proton irradiation of CO/H<sub>2</sub>O ices produces CO<sub>2</sub>. This is seen in Fig. 4, where the sublimation curves for unirradiated and irradiated CO/H<sub>2</sub>O ices (ratio = 0.14) are compared, the latter showing both CO and CO<sub>2</sub> release. From the preceding discussion on unirradiated CO/H<sub>2</sub>O ice, it will be recalled that the relative intensities of the two highest temperature CO releases are reversed as the CO/H<sub>2</sub>O ratio is decreased (Fig. 2). Figure 4 shows a comparable change brought about by ionizing radiation. The radiation converts some of the CO in the ice into CO<sub>2</sub>, effectively dropping the CO/H<sub>2</sub>O ratio and changing the relative intensities of the two highest temperature CO releases. In each case studied, an ice with some given CO/

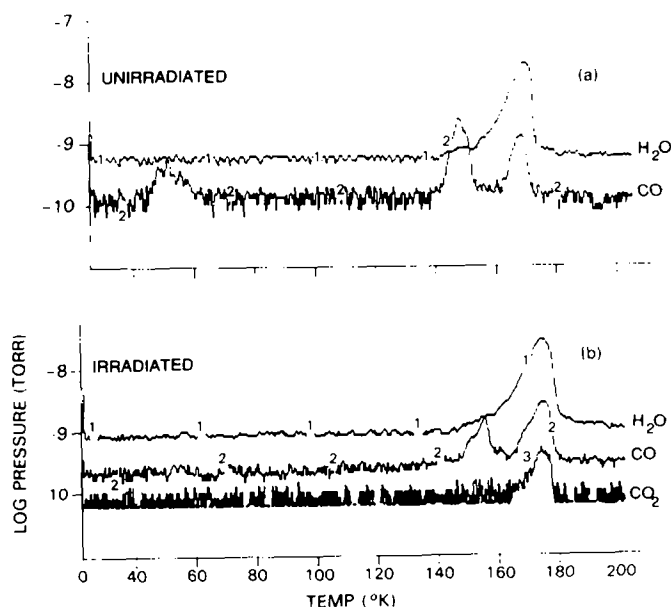


FIG. 4. Effect of proton irradiation at 28 K on the sublimation of a 0.5- $\mu\text{m}$  film of CO/H<sub>2</sub>O ice deposited at 28 K. CO/H<sub>2</sub>O = 0.14 for both runs shown.

H<sub>2</sub>O ratio was changed by the radiation so as to produce a sublimation curve characteristic of a smaller CO/H<sub>2</sub>O ratio.

Radiation experiments were also carried out on CO<sub>2</sub>/H<sub>2</sub>O ices. IR spectra recorded before and after irradiation showed CO<sub>2</sub> loss and CO formation, as expected. The analysis of CO<sub>2</sub>/H<sub>2</sub>O radiation results was complicated by the fact that CO<sub>2</sub> undergoes fragmentation in a mass spectrometer to produce CO, so that even unirradiated CO<sub>2</sub>/H<sub>2</sub>O ices appear to show some CO release. By comparing sublimation curves from unirradiated and irradiated CO<sub>2</sub>/H<sub>2</sub>O samples, it was found that the irradiated samples produced a mass spectral signal for CO about five times greater than the unirradiated ones. Irradiated CO<sub>2</sub>/H<sub>2</sub>O samples always released CO and CO<sub>2</sub> at the same temperatures.

## DISCUSSION

### Unirradiated Ices

Gas release occurred from Ar/H<sub>2</sub>O and CO/H<sub>2</sub>O ices in five temperature regions as shown in Fig. 2. Although these have been the subject of earlier study (e.g., Bar-Nun *et al.* 1985, 1987), our use of IR spectroscopy in conjunction with mass spectrometry justifies some discussion of each gas release.

Since the IR absorptions of H<sub>2</sub>O in the ices were unchanged before and after gas release I, we believe that it

was primarily from gas on the ice surface, in agreement with Bar-Nun *et al.* 1987). In contrast, Sandford and Allamandola (1988), looking at only the solid phase, assigned the first release to gas escaping from interstitial sites in the H<sub>2</sub>O ice. It is possible that both processes may be taking place simultaneously.

As the sample was warmed through region II, the IR absorptions of H<sub>2</sub>O shifted, and so we assign the second release to annealing of the amorphous H<sub>2</sub>O and not simply the sublimation of a monolayer of gas (Bar-Nun *et al.* 1987). This release may be due to gas escaping from interstitial sites in the H<sub>2</sub>O ice as mentioned above. We also assign gas release III to an annealing process since we observed small shifts in the IR absorptions of H<sub>2</sub>O in this region.

Gas releases IV and V, for  $T > \sim 130$  K, are assigned to crystallization of the amorphous ice and to the sublimation of the crystalline ice, respectively. Our work establishes both of these assignments unequivocally as we are able to see the characteristic shifts of the IR bands of H<sub>2</sub>O at the phase change and the loss of all IR bands at the higher temperature.

We know of only one sublimation experiment in which a CO<sub>2</sub>/H<sub>2</sub>O ice, prepared by codeposition, was studied with mass spectrometry (Bar-Nun *et al.* 1985, experiment 17). The results reported are similar to ours for the same CO<sub>2</sub>/H<sub>2</sub>O value (3/1). However, the authors' nonobservation of CO<sub>2</sub> release around 175 K, combined with the observation of release at that temperature in Ar/H<sub>2</sub>O and CO/H<sub>2</sub>O ices, was used as part of their argument for clathrate hydrate formation in Ar/H<sub>2</sub>O and CO/H<sub>2</sub>O ices but not in CO<sub>2</sub>/H<sub>2</sub>O. From our Fig. 3 it is clear that whether or not this final release of CO<sub>2</sub> is seen depends strongly on the ice's CO<sub>2</sub>/H<sub>2</sub>O ratio. Claims concerning clathrate hydrates based primarily on a single CO<sub>2</sub>/H<sub>2</sub>O ratio must be viewed with caution (see also Kouchi 1990).

Our results are in good agreement with, and in fact complement, the detailed IR studies of Sandford and Allamandola (1988, 1990). For example, they observed two CO absorptions in CO/H<sub>2</sub>O ices, one assigned to substitutionally trapped CO, the other to interstitially trapped CO. As the sample was annealed, the interstitial CO was removed by  $\sim 80$  K, leaving only substitutional CO. However, it was not clear if the interstitial CO was converted into the other type or actually being lost by sublimation. Our mass spectral observations of Ar/H<sub>2</sub>O and CO/H<sub>2</sub>O ices showed gas release between 50 and 80 K (region II of Fig. 2) so presumably some interstitial CO is subliming. In a different experiment, Sandford and Allamandola found "No measurable loss of H<sub>2</sub>O" for ices with CO/H<sub>2</sub>O = 0.05 held at 125 K for 21 hr. Our mass spectral experiments gave only a trace of H<sub>2</sub>O released under 125 K for a ratio of 0.07. Finally, Sandford and Allaman-

dola (1988), using only IR, find CO sublimation mainly in temperature regions I, IV, and V of our Fig. 2. The use of mass spectrometry allowed us to detect CO directly in the vapor state in those three regions but also in regions II and III. Since we found that gas release in these regions increased monotonically with the initial CO/H<sub>2</sub>O ratio, it is not surprising that IR studies alone of a CO/H<sub>2</sub>O = 0.05 ice did not detect CO loss.

In another extensive study, Sandford and Allamandola (1990) followed sublimation from CO<sub>2</sub>/H<sub>2</sub>O ices by intensity changes in the  $\nu_2$  IR band of CO<sub>2</sub> ( $\approx 2340$  cm<sup>-1</sup>). Our results agree with theirs, that CO<sub>2</sub> release is strongly dependent on the initial CO<sub>2</sub>/H<sub>2</sub>O ratio. Figure 3a shows that a ratio of 3 gave CO<sub>2</sub> sublimation beginning at almost the same temperature as in pure CO<sub>2</sub>, namely  $\sim 80$  K. Some H<sub>2</sub>O was carried off at this temperature as well. However, as the initial gas concentration is dropped (Figs. 3b and 3c) the sublimation curves begin to resemble Fig. 2c for Ar/H<sub>2</sub>O, and CO/H<sub>2</sub>O, ices. In these cases it is H<sub>2</sub>O that is controlling gas sublimation at temperatures above  $\sim 80$  K. The cometary implications of these results have been discussed in detail (Sandford and Allamandola 1990).

#### Irradiated Ices

The significant results from our radiation experiments come from CO/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>O ices. In both systems, IR spectroscopy and mass spectrometry provided evidence of chemical reactions and product sublimation. In all ices, the product molecule was released concurrently with the parent, as shown in Fig. 4. Neither the radiation nor the presence of the third (product) molecular species altered the observation of gas release in well-defined temperature regions.

It is also worth noting that since the amount of gas released at different temperatures is concentration dependent (Figs. 2 and 3) and since ionizing radiation alters concentrations, then exposure to radiation will change the relative amounts of gas released from ices at various temperatures.

#### Astrophysical Implications

The primary astrophysical implication of our work on ices is for models of comet sublimation. All models that assume gases are released from a comet's nucleus continuously, starting at each gas's sublimation temperature, are incorrect. First, models must allow for the fact that the sublimation of cometary gases, such as CO, will carry away water at temperatures far below that for H<sub>2</sub>O sublimation. Second, models must include the dependence of the quantity of gas released at any temperature on the gas concentration in the frozen nucleus. Third, the release of many different cometary gases in the same temperature region must be recognized.

Our radiation chemical experiments on CO/H<sub>2</sub>O and CO<sub>2</sub>/H<sub>2</sub>O ices are also relevant to cometary science. In our experiments, irradiated CO/H<sub>2</sub>O ice produced CO<sub>2</sub> which was subsequently released at the same temperatures as CO. This implies that the CO in a cometary nucleus, when subjected to cosmic radiation, will produce CO<sub>2</sub> and that the two gases can be released at the same temperatures. The statement of Feldman *et al.* (1986) that "it is likely that both species are released simultaneously during the [cometary] outbursts" is supported by our laboratory studies of cometary ices.

Much work remains in extending and quantifying our sublimation experiments. In particular, our use of IR to aid in the interpretation of mass spectral results and mass spectrometry to detect gas releases missed by IR is promising. There is also a need for more ice experiments involving ionizing radiation.

#### ACKNOWLEDGMENTS

Marla Moore is acknowledged for invaluable assistance with many experimental problems. Raj Khanna of the University of Maryland is thanked for discussions involving IR spectroscopy. L. Allamandola is thanked for copies of useful papers (reprints and preprints) and especially for many comments which have improved this paper. A. Bar-Nun's comments on an early draft of this paper are also acknowledged. R.L.H. was supported by NASA grant NAG 5-952 and by an Intergovernmental Personnel Act Agreement. Eckerd College is acknowledged for a leave-of-absence to R.L.H. to carry out this research.

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