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# SOLID-PHASE FORMATION OF INTERSTELLAR VINYL ALCOHOL

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## ABSTRACT

Motivated by the recent discovery of gas-phase interstellar vinyl alcohol, $CH_2{=}CH(OH)$, we present laboratory experiments on this molecule's solid-phase formation. Through a combination of reaction chemistry, infrared spectroscopy, isotopic substitution, thermal annealings, and independent syntheses, we have identified vinyl alcohol in proton-irradiated $H_2O + C_2H_2$ ices and have measured its column density at ∼15 K. UV photolysis of $H_2O + C_2H_2$ ices at ∼15 K also produces vinyl alcohol. It is suggested that vinyl alcohol is formed in interstellar ices and then ejected into the gas phase, where it might undergo additional reactions.

*Subject headings:* ISM: molecules — line: formation — line: identification — molecular processes

## 1. INTRODUCTION

The discovery of polyatomic organic molecules at radio, microwave, and infrared frequencies continues to present challenges to astrochemists. While the production of some molecules is successfully explained by gas-phase models, others appear to require solid-phase formation on icy mantles of interstellar grains. For example, solid-phase chemistry has been invoked to explain gas-phase interstellar observations of formaldehyde (Federman & Allen 1991), acetic acid (Mehringer, Snyder, & Miao 1997), ethylene oxide (EO; Nummelin et al. 1998), methylenimine (Dickens et al. 1997), ethyl cyanide (Miao & Snyder 1997), and methanol (e.g., Charnley et al. 1995).

Vinyl alcohol [VA; $CH_2{=}CH(OH)$] is yet another molecule for which a solid-phase source may be needed. Turner & Apponi (2001) recently reported microwave observations of VA toward Sgr B2N, a molecular cloud. In their paper, they not only considered a gas-phase formation mechanism but also the possibility that VA synthesis could be catalyzed on grains. Once made and subsequently ejected from a grain, VA might then isomerize to EO ($c$-$C_2H_4O$) and acetaldehyde [AC; $CH_3C({=}O)H$], both interstellar molecules.

A key part of the above scenario is the solid-phase formation of VA. Although conventional wisdom has long held (Erlenmeyer 1881) that VA is unstable and isomerizes into AC, VA has indeed been synthesized (Saito 1976) and, under the right conditions, possesses a surprising and useful stability (Capon et al. 1988). Nevertheless, laboratory preparations of VA typically employ chemical precursors unlikely to be interstellar molecules, and reactions unlikely in the interstellar medium (ISM).

In this Letter, we outline a different approach for VA formation, one that is applicable to interstellar conditions. We demonstrate that VA can be readily synthesized in *ices* from known interstellar molecules, by either cosmic-ray bombardment or exposure to far-UV (or higher energy) photons. Although VA still cannot be "bottled and sold," energetic processing in the ISM can easily make this rather elusive organic molecule.

## 2. EXPERIMENTAL

Our experimental procedures are already in print, so we present only a summary here. Additional information can be found in, for example, Hudson, Moore, & Gerakines (2001) and Moore & Hudson (2000).

Chemical reagents for experiments were purchased largely from Aldrich, Matheson, and Cambridge Isotopes. Ice samples typically were prepared by vapor-phase condensation onto a precooled (∼15 K) aluminum substrate in a high-vacuum chamber. Ice thicknesses of several micrometers were reached in about 1 hr, with thicknesses being measured with a laser interference system. In some experiments, ices were made by injecting a room-temperature liquid-phase solution onto a precooled substrate.

Ices were irradiated with 0.8 MeV protons from a Van de Graaff accelerator to doses of 5–25 eV per 18 amu molecule. For the use of proton radiolysis to mimic cosmic-ray bombardment, see Moore, Hudson, & Gerakines (2001). Since sample thicknesses were on the order of a few micrometers, the incident protons, having a range of 16 $\mu$m (Northcliffe & Shilling 1970), penetrated the ices and came to rest in the underlying metal substrate, not in the ices themselves. Far-UV photolyses were performed with a microwave-discharge hydrogen-flow lamp producing primarily Ly$\alpha$ photons (10.2 eV, 121.6 nm, and $\sim 3.1 \times 10^{14}$ photons $cm^{-2}$ $s^{-1}$). For more on the UV technique, see Gerakines, Moore, & Hudson (2000) and Allamandola, Sandford, & Valero (1988).

Infrared (IR) spectra of ices were recorded as 60-scan accumulations before and after exposure to the proton beam (or UV lamp), typically at a resolution of 4 $cm^{-1}$ from 4000 to 400 $cm^{-1}$. Converting an IR band's integrated intensity $\int \tau(\tilde{\nu})d\tilde{\nu}$, in units of $cm^{-1}$, to a molecular column density $N$, in units of molecules $cm^{-2}$, is possible through

$$N = \frac{\int \tau(\tilde{\nu})d\tilde{\nu}}{A},$$

where $A$ is the band's intrinsic strength, in units of cm molecule$^{-1}$ (Hudgins et al. 1993).

## 3. RESULTS

Figure 1 shows IR spectra of an $H_2O + C_2H_2$ mixture (4 : 1) before (Fig. 1*a*) and after (Figs. 1*b*–1*d*) proton radiolysis. Most of the spectral features already have been assigned (Moore & Hudson 1998). What has not been previously assigned is the strong band, marked with an asterisk, appearing near 1145 $cm^{-1}$ after irradiation. Although this band's growth appears to correlate with an increase in a C═O stretch near

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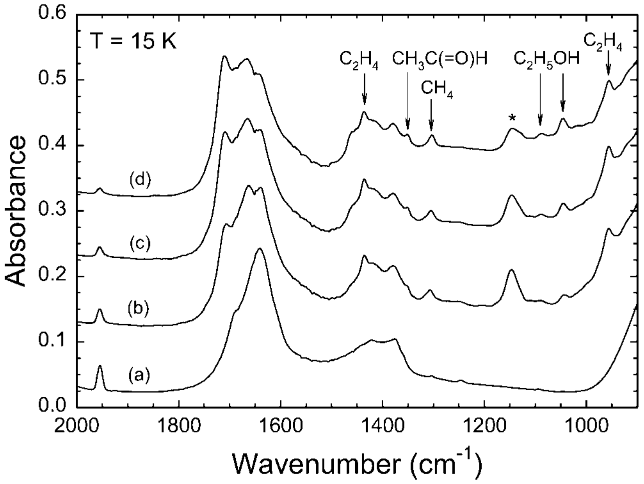

FIG. 1.—IR spectra of $H_2O + C_2H_2$ (4 : 1) at 15 K (*a*) before irradiation and after doses of about (*b*) 5.2 eV molecule$^{-1}$, (*c*) 11 eV molecule$^{-1}$, and (*d*) 18 eV molecule$^{-1}$.

1700 cm$^{-1}$, the later band continues to increase in the final spectrum of Figure 1*d* even though the 1145 cm$^{-1}$ band decreases. In fact, the feature growing near 1700 cm$^{-1}$ is correlated with a smaller feature near 1350 cm$^{-1}$, as a result of AC (Moore & Hudson 1998). Figure 2 shows the rise and fall of the 1145 cm$^{-1}$ feature with increasing radiation dose. For convenience, we now anticipate our spectral assignment (see § 4) and simply state that the IR band near 1145 cm$^{-1}$ shown in Figures 1*b*–1*d* is due to the $\nu_9$ (C—O stretch) VA. Many experiments were performed to test this assignment, and these are now briefly described.

### 3.1. *Sample Composition*

Irradiations of $H_2O + C_2H_2$ mixtures with concentration ratios from 15 : 1 to 1 : 3 all gave the 1145 cm$^{-1}$ band. This feature also was observed after irradiation of $H_2O$-dominated ices made of $H_2O + C_2H_2 + CO$, $H_2O + C_2H_2 + CH_4$, and $H_2O + C_2H_2 + CO + CH_4$. Numerous "blanks" were done to ensure that the 1145 cm$^{-1}$ absorbance was due to a reaction involving $H_2O + C_2H_2$. These included experiments with pure $H_2O$, pure $C_2H_2$, and binary mixtures of either $H_2O$ or $C_2H_2$ and common laboratory contaminants (e.g., $N_2$, $O_2$, $CH_4$, $CH_3OH$, and $NH_3$). None of these experiments produced the 1145 cm$^{-1}$ band.

### 3.2. *Isotopic Substitution*

The VA 1145 cm$^{-1}$ feature was shifted to 1127 cm$^{-1}$ on irradiation of a $H_2O + {}^{13}C_2H_2$ mixture (5 : 1). Correlated with this peak was a new one at 1589 cm$^{-1}$. Also, the VA 1145 cm$^{-1}$ band was shifted to 966 cm$^{-1}$ after irradiation of $D_2O + C_2D_2$ (5 : 1) and correlated with a new band at 1581 cm$^{-1}$. The bands appearing at 1589 and 1581 cm$^{-1}$ after irradiations of $H_2O + {}^{13}C_2H_2$ and $D_2O + C_2D_2$ mixtures, respectively, agree with the published $\nu_5$ (C=C stretch) frequencies of VA isotopomers (Hawkins & Andrews 1983).

### 3.3. *Alternate Syntheses*

The 1145 cm$^{-1}$ band also was observed after UV photolysis of $H_2O + C_2H_2$ ices for 1 hr. Photolysis of an ion-irradiated sample caused the 1145 cm$^{-1}$ band to go through the same type of rise and fall shown in Figure 2.

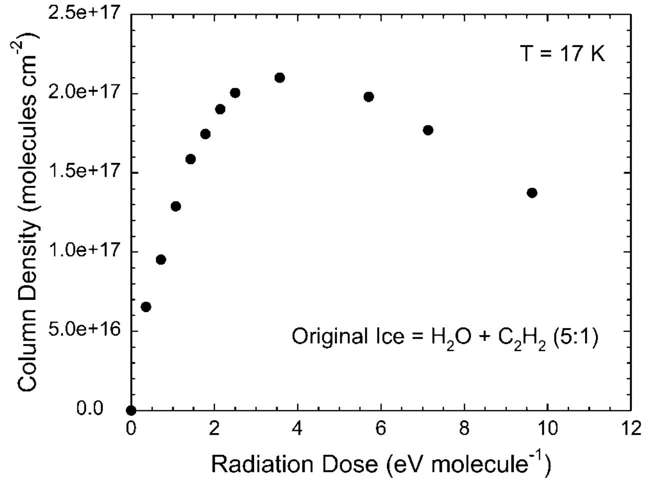

FIG. 2.—Growth and decay of the 1145 cm$^{-1}$ VA band during irradiation of $H_2O + C_2H_2$ (5 : 1) at 17 K.

Kunttu et al. (1988) showed that UV photolysis of vinyl formate produces CO and VA according to the following reaction:

$$CH_2CHOC(O)H \rightarrow CH_2CH(OH) + CO.$$

We used this reaction to prepare VA in $H_2O$ ice. Figure 3 shows IR spectra before (Fig. 3*a*) and after (Fig. 3*b*) irradiation of a $H_2O + C_2H_2$ mixture (15 : 1). Bands of an irradiated sample of $H_2O$ + vinyl formate are shown in Figure 3*c*. The resemblance of the authentic VA band near 1145 cm$^{-1}$ in Figure 3*c* to the one in our $H_2O + C_2H_2$ ice is obvious.

We observed a band near 1145 cm$^{-1}$ in other irradiated $H_2O$-rich ices, and these will be described in a future paper. The mixtures studied to date include $H_2O + C_2H_4$, $H_2O + C_2H_5OH$, $H_2O$ + EO, $H_2O$ + AC, $H_2O + CH_2(Cl)CH_2(OH)$, and $H_2O + CH_2(OH)CH_2(OH)$.

### 3.4. *Temperature Effects*

When an irradiated $H_2O + C_2H_2$ (5 : 1) ice was warmed, the 1145 cm$^{-1}$ feature remained essentially unaltered up to ~170 K. At this temperature, $H_2O$ sublimes away in our vacuum

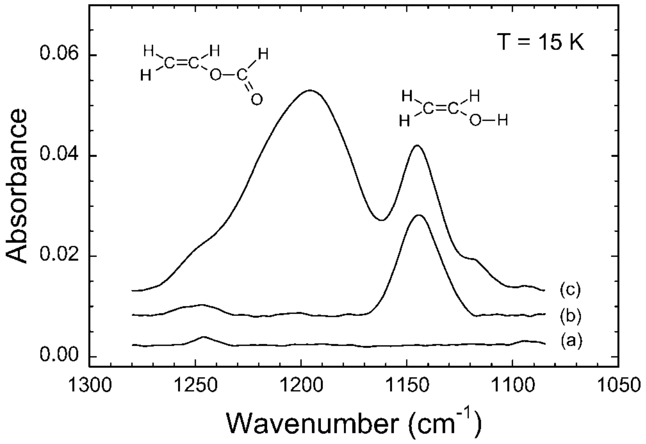

FIG. 3.—Spectra of a $H_2O + C_2H_2$ (4 : 1) mixture at 15 K (*a*) before and (*b*) after irradiation, compared with (*c*) the spectrum of irradiated $H_2O$ + vinyl formate (20 : 1). Before irradiation, neither mixture's spectrum displayed the large band at 1145 cm$^{-1}$.

system, so the 1145 $cm^{-1}$ band and all remaining IR features were lost as their carriers left with the sublimating $H_2O$.

The VA band was produced not only by irradiation at ~15 K but also at 80 K. No other temperatures have been investigated, and no quantitative comparisons of yields have yet been made.

### 3.5. *Other Experiments and Observations*

Since Figure 2 shows that VA is destroyed on continued irradiation, we sought to observe a decomposition product. Hawkins & Andrews (1983) reported that $H_2C{=}C{=}O$, ketene, results from decomposition of VA, but the strongest ketene band overlaps with an intense CO band near 2140 $cm^{-1}$. To circumvent this problem, we used isotopic labeling to separate the ketene feature from CO. After proton irradiation of $H_2O + {}^{13}C_2H_2$ ices, we indeed detected $H_2^{13}C^{13}CO$, at 2071 $cm^{-1}$. Similarly, after irradiation of $D_2O + C_2D_2$, we detected $D_2C{=}C{=}O$, at 2117 $cm^{-1}$. These ketene identifications were made by comparisons with authentic samples, prepared according to the method of Haller & Pimentel (1962) with the appropriate starting materials.

Two other types of experiments were done to support our work. In the first, as an estimate for the C−O band strength of VA, we measured the *A*-value of the C−O stretch in methylvinyl ether, $CH_2{=}CH(OCH_3)$, as $A(1208\ cm^{-1}) = 6.0 \times 10^{-18}$ cm $molecule^{-1}$. With this band strength, and with $A(C_2H_2, 1956\ cm^{-1}) = 3.19 \times 10^{-19}$ cm $molecule^{-1}$ (Hudson & Moore 1997), we calculated an acetylene-to-VA conversion of about 43% for the highest point (~3.5 eV $molecule^{-1}$) in Figure 2. In the second type of experiment, we measured the C−O stretching frequencies of ${}^{12}CH_3OH$ (1016 $cm^{-1}$) and ${}^{13}CH_3OH$ (994 $cm^{-1}$), made by proton irradiating $H_2O + {}^{12}CO$ and $H_2O + {}^{13}CO$, respectively, at ~15 K. This shift was used to predict the ${}^{13}C$ shift of VA's $\nu_9$ band.

## 4. DISCUSSION

### 4.1. *Spectral Assignment*

The 1145 $cm^{-1}$ band's early appearance and prominence during radiolysis of the $H_2O + C_2H_2$ mixture (Fig. 1) suggest that it is due to a primary reaction product of $H_2O$ and $C_2H_2$. Since one of the main channels for radiolytic and photolytic decomposition of $H_2O$ gives H atoms and OH radicals, then reaction of $C_2H_2$ with H and/or OH is expected. As reported earlier (Hudson & Moore 1997; Moore & Hudson 1998), ethane and ethanol are produced in irradiated $H_2O + C_2H_2$ mixtures, the sequence being as follows:

$$HCCH \rightarrow H_2CCH_2 \rightarrow H_3CCH_3.$$

For ethanol formation, the reaction path

$$HCCH \rightarrow ?? \rightarrow H_3CCH_2OH$$

requires an intermediate, VA being one candidate. Thus, the radiation chemistry of the $H_2O + C_2H_2$ system suggests

$$HCCH \rightarrow CH_2CH(OH) \rightarrow H_3CCH_2OH,$$

with VA as the intermediate molecule.

Additional support for the VA assignment is the lack of other strong unassigned bands in the spectrum and the thermal behavior of the 1145 $cm^{-1}$ feature. That the band persists until 170 K indicates that it is not from a small, volatile molecule, such as $CH_4$, nor is it due to a free radical. The lack of additional strong bands excludes the aldehyde, ketone, acid, ester, and hydrocarbon classes of organics, leaving only ethers and alcohols. The 1145 $cm^{-1}$ position is reasonable for a C−O stretching vibration of either an organic ether or an alcohol, but no ether has its most prominent IR band at this position. This leaves only an alcohol, other than methanol and ethanol, as a possibility. Again, VA suggests itself.

VA has been made in the past by pyrolysis of larger compounds, such as 2-chloroethanol (Joo, Merer, & Clouthier 1999), UV photolysis of vinyl formate (Kunttu et al. 1988), and UV photolysis of $O_3 + C_2H_4$ in an argon matrix (Hawkins & Andrews 1983). These experiments all show that VA has an intense IR absorption around 1100 $cm^{-1}$, corresponding to its $\nu_9$ vibration. This is exactly the spectral region where we see a prominent band in our own experiments, as shown in Figure 1.

The frequency shifts in our ${}^{13}C$- and deuterium-substitution experiments are consistent with this interpretation. Hawkins & Andrews (1983) found that the $\nu_9$ VA band is essentially a C−O vibration. This means that the 20 $cm^{-1}$ ${}^{13}C$ shift we see is reasonable for VA in going from ${}^{12}C{-}O$ to ${}^{13}C{-}O$, since this is approximately the difference in C−O stretching frequencies we observed between ${}^{12}CH_3OH$ and ${}^{13}CH_3OH$. Our deuterium shift was slightly (~10%) higher than that reported by Hawkins & Andrews (1983) but reasonable given the drastic change in going from their rare-gas matrix to our $D_2O$ environment for a hydrogen-bonded molecule.

Yet another approach we used to assign the 1145 $cm^{-1}$ feature to VA was to generate this molecule by an independent path. This was done with irradiations of vinyl formate. Figure 3 shows the good agreement achieved.

To summarize, our VA assignment is supported by five lines of thought: (1) the chemistry of the $H_2O + C_2H_2$ system, (2) the thermal behavior of the 1145 $cm^{-1}$ band, (3) the band's spectral position, (4) both the ${}^{13}C$ and deuterium shifts, and (5) comparisons of the band with a reference spectrum of VA. Strictly speaking, only the *syn* conformer of VA has been studied (see Rodler & Bauder 1984).

Having assigned the strong 1145 $cm^{-1}$ band to VA, we now consider other IR features of this molecule in $H_2O$-rich ice. It is expected that the 1145 $cm^{-1}$ band's shift from ~1100 $cm^{-1}$ in the gas phase is due to hydrogen bonding between VA's oxygen atom and the $H_2O$ ice. However, most other vibrations will show little or no such perturbation, so we can expect them closer to their gas-phase values. Unfortunately, the other VA bands are either weaker than the one at 1145 $cm^{-1}$, overlap with one of the strong features of $H_2O$ ice around 3300, 1660, and 760 $cm^{-1}$, or both. Our two isotopic-substitution experiments circumvented this problem for the VA $\nu_5(C{=}C)$ band near 1650 $cm^{-1}$. Irradiating $H_2O + {}^{13}C_2H_2$ produced ${}^{13}C$-labeled VA with the $\nu_5(C{=}C)$ band shifted to 1589 $cm^{-1}$, out from under the adjacent $H_2O$ feature. A similar experiment separated the $\nu_5$ band of deuterated VA from $D_2O$.

### 4.2. *Relationship to Previous Work*

The work most closely related to that presented here is our own and that of Wu et al. (2002). In an earlier paper on $H_2O + C_2H_2$, we mentioned VA in passing, and an unassigned 1145 $cm^{-1}$ band was shown (see Figs. 5 and 7 in Moore & Hudson 1998). In photochemical work on $H_2O + C_2H_2$ mixtures, this same band was left unidentified and labeled as "?" (see Figs. 3 and 10 in Wu et al. 2002).

Our observation of VA at ~170 K is consistent with ab initio molecular orbital calculations of its stability by Smith et al. (1991). An examination of their potential energy surface for $C_2H_4O$ isomers gives the activation energy for the VA-to-AC rearrangement as 235 kJ $mol^{-1}$ ($= 2.44$ eV). This implies that once VA is formed by radiolysis near 15 K, it will be stable in the solid state on laboratory timescales, barring additional photochemical and radiation damage.

### 4.3. *Astrochemical Considerations*

Our experiments demonstrate that ice processing by cosmic rays or UV photons can easily make VA from $H_2O$ and $C_2H_2$, both known interstellar molecules. Our experiments also show that VA is produced not only in binary mixtures but in more complex ones as well, at ∼15 K and higher, and by both radiolysis and photolysis. All of this argues for the ease with which VA can be synthesized. That VA was seen up to 170 K suggests that once formed, it can indeed remain intact in an icy grain mantle prior to release into the gas phase.

Beyond these considerations, it is difficult to predict a gas-phase VA abundance from our solid-phase work. The VA formation rate is related to the radiation dose, or photolytic exposure, received by the parent ice. Doses in our experiments were 1–20 eV $molecule^{-1}$. For comparison, the dose to the outer 0.02 $\mu$m of an ice grain in a cold, dense interstellar cloud is estimated to be ∼3 eV $molecule^{-1}$ over $10^7$ yr (Moore et al. 2001). Strazzulla & Johnson (1991) calculated that ices of Oort cloud comets receive ∼5 eV $molecule^{-1}$ at 5 m beneath a nuclear surface, integrated over the age of the solar system, with higher doses at smaller depths and vice versa.

Although we have identified VA in an irradiated laboratory ice, direct observation of VA in an *interstellar* ice could be challenging. *Infrared Space Observatory* spectra of embedded protostars, such as IRS 9 and W33A, show intense IR absorbances from interstellar silicates and $H_2O$ ice in precisely the spectral regions of VA's strongest bands (Gibb et al. 2000). More optimistically, to the degree that cometary ices reflect the composition of interstellar material, cometary comae may be much better sources for new VA detections.

Finally, we observe that Turner & Apponi (2001) detected VA in the Sgr B2N system, the same region where Hollis et al. (2002) recently found ethylene glycol, $HO-CH_2-CH_2-OH$. The astrochemical relationship between VA and ethylene glycol, and other molecules, remains to be explored.

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