

Recent results from the Leiden Observatory Laboratory : (a) band strengths in mixed ices ; (b) UV photolysis of solid methanol

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Received 10 October 1994; revised 27 December 1994; accepted 5 January 1995

Abstract. We review the recent work done in the Leiden Observatory Laboratory on measuring the IR band strengths of CO and CO₂ diluted in various binary ice mixtures. These measurements were performed with a novel technique in which the component gases are deposited simultaneously through separate tubes, avoiding a number of pitfalls intrinsic in previous methods where the components were premixed in a gas container before deposition. The error in the new method is in general only a few percent. We also review the results on the UV photolysis of solid methanol at 10 K. By starting the IR spectroscopic monitoring after very small UV doses (i.e. 6 s), we clearly distinguish the first order photolysis products, i.e. H₂CO, CH₄, HCO and H₂, from the higher order products, i.e. CO and CO₂.

Introduction

To derive column densities from the equivalent widths of the IR absorption bands of species in interstellar icy grain mantles, reliable measurements of the IR band strengths under astrophysically relevant conditions are required. Besides very low temperatures (~ 10 K), such conditions involve dilution of the molecules by other species present in the interstellar ices. In the first part of this paper we report measurements of the band strengths for CO and CO₂ in low temperature matrices of various astrophysically relevant ice materials. It has been shown that these species are important constituents of interstellar icy grain mantles (Whittet *et al.*, 1985; Tielens *et al.*, 1991; d'Hendecourt and Jourdain de Muizon, 1989).

In the second part of our paper we report the results of the UV photolysis of methanol ice at 10 K. This molecule

has been detected in ices in various lines-of-sight through the dense cloud medium (Grim *et al.*, 1991; Allamandola *et al.*, 1992; Skinner *et al.*, 1992). Understanding its photochemistry could therefore be of importance for understanding the evolution of icy grain mantles in dense clouds. The photochemistry of methanol has been studied previously in complex ice mixture analogues for the ice mantles observed in the dense medium (Allamandola *et al.*, 1988). Here we aim at a more fundamental understanding by investigating the photochemistry of the pure ice. To be useful for the interpretation of astrophysical data, careful *in situ* IR monitoring of the abundances of the various photolysis products as a function of irradiation dose is desirable. In particular, first and higher order products of the photolysis should be distinguished by measuring the production rates at very low dose.

Experimental techniques

Our equipment for producing interstellar ice analogues is similar to those described previously (Hagen *et al.*, 1979; Hudgins *et al.*, 1993). It consists of a vacuum chamber with a cold finger on which a substrate holder is mounted with a CsI window substrate which can be cooled to 10 K. Ice samples are prepared by deposition of gases on the substrate through a deposition tube. The set-up is equipped with two such deposition tubes. To enable *in situ* IR transmission spectroscopy, the vacuum chamber is placed in the sample compartment of an IR spectrometer (Bio-Rad FTS 40-A) such that the IR beam enters and leaves the chamber through two KBr windows and passes through the substrate at right angles. A hydrogen discharge lamp is mounted on a third window consisting of MgF₂, enabling vacuum UV photolysis of the ice samples.

Our method of measuring the band strengths of species in binary ice mixtures involved the separate deposition of the component gases through the two deposition tubes in

our set-up. The deposition of the subject gas (i.e. the species for which the band strengths are to be measured) was made twice, first by itself, resulting in the formation of a pure sample, and next with simultaneous independent deposition of the amount of diluting material required to obtain the desired binary ice mixture. In both cases the deposited quantity of subject material was kept equal. Therefore, the ratio of a band strength in the pure ice to that in the binary ice is simply equal to the ratio of the integrated absorbances. Using the value for the band strength in pure ice from the literature, the band strength in the mixed ice can then be obtained.

Our method involving separate deposition of the component materials avoids a number of pitfalls inherent in earlier determinations of band strengths in mixed ices, in which the component gases were pre-mixed in a gas container and deposited together. Factors that could cause errors in this case are incomplete mixing of the gases, variation in the thermal molecular velocities if molecules of widely varying mass are employed, and the presence of reservoirs of species stuck on the walls of the container if gases of limited volatility are used close to their vapour pressures.

In the case of UV photolysis, the thickness of the ice sample was less than or equal to $0.1 \mu\text{m}$, to ensure it being optically thin to UV radiation.

Band strengths in mixed ices

Table 1 shows the strengths of the main IR bands of CO and CO₂, when diluted in various species at a ratio of 20 : 1. For comparison, previous estimates of the band strengths are also given. The accuracy of our results is in general only limited by the reproducibility of the deposition, which was experimentally determined to be better than 3 %. In some cases a larger error was created by the uncertainty in setting the baseline, i.e. when the feature lies on top of a band related to the matrix material. In that case

Table 1. Band intensities for CO and CO₂ in various matrices (dilution 20: 1, "pure" denotes the undiluted ice)

Molecule	Feature (μm)	Matrix	σ_{int} (new) (cm mol ⁻¹)	σ_{int} (old)* (cm mol ⁻¹)
CO	4.68	pure	1.1 (-17) [†]	
		H ₂ O	1.1 (-17)	1.7 (-17)
		O ₂	1.1 (-17)	
		CO ₂	1.1 (-17)	
CO ₂	4.27	pure	7.6 (-17) [‡]	
		H ₂ O	7.1 (-17)	2.1 (-16)
		GO	8.3 (-17)	7.4 (-17)
		O ₂	7.2 (-17)	
	15.2	pure	1.1 (-17)	
	H ₂ O	1.5 ± 0.2 (-17)	4.1 (-17)	
	CO	1.1 (-17)	7.6 (-18)	
	O ₂	9.4 (-18)		

* Sandford et al. (1988), Sandford and Allamandola (1990).

[†] Jiang et al. (1975).

[‡] Yamada and Person (1964).

a value for the error is quoted in the table as determined by using various polynomial baseline fits.

It can be seen from Table 1 that the variation of the band strengths for CO and CO₂ between various matrices is quite limited, i.e. below -20%. This is remarkable in view of the often large differences in band shapes and widths in these matrices, e.g. the $4.68 \mu\text{m}$ CO feature has a three-fold larger width when diluted in water ice relative to the pure ice (Sandford et al., 1988), but the corresponding band strengths are found to be equal. The large differences between our band strength measurements and previous values of up to almost a factor of 3 reflect the difficulties in controlling the composition of the deposited gas mixtures relating to the pitfalls described in the previous section.

Our results have a number of astrophysical implications. First, the considerably lower values that we find for the band strengths of CO and CO₂, diluted in H₂O ice as compared to previous measurements imply that the abundance of CO and CO₂ in interstellar ices has been underestimated. For CO, the improved estimates are not very different from the previous values, since this molecule is mostly present in apolar ice material (Sandford et al., 1988), for which the new values are not different from the previous ones. For CO₂, the interstellar abundance was previously determined from the observed $15.2 \mu\text{m}$ feature, using the old value of the band strength in an H₂O matrix of $4.1 \times 10^{-17} \text{ cm mol}^{-1}$ (d'Hendecourt and Jourdain de Muizon, 1989). The new values result in 2.7-3.7-fold higher estimates, depending on which ice matrix is adopted. This implies the presence of up to $\sim 10\%$ CO₂ relative to H₂O in dense cloud ices.

UV photolysis of solid methanol; results

Figure 1 shows the IR spectrum of a $0.12 \mu\text{m}$ film of methanol ice directly after deposition and after 10 min of UV photolysis. The applied Philips hydrogen flow dis-

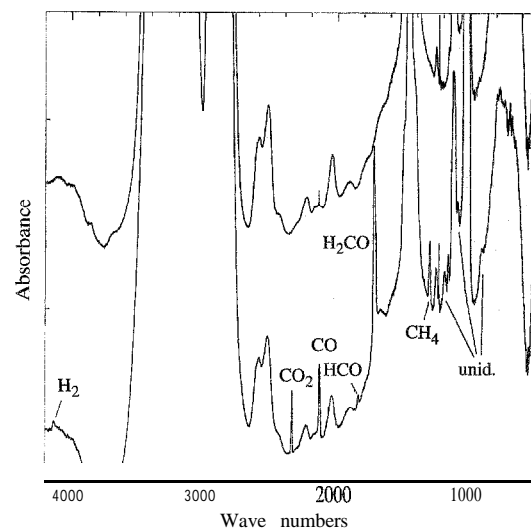


Fig. 1. (Upper curve) IR spectrum of the methanol samples directly after deposition. (Lower curve) IR spectrum of the sample after 10 min. UV photolysis (equivalent to 4×10^7 years of processing inside a dense cloud; see text)

Table 2. New features with their identifications; abundances after 1 h UV photolysis are given relative to the amount of methanol before photolysis; column 3 gives the applied band strengths

Molecule	Feature(s) (cm ⁻¹)	σ_{int} (cm mol ⁻¹)	Abund. (%)	Ref.*
CH ₃ OH	1026	1.8 (-17)	65.7	1
H ₂ CO	1725.5	9.6 (-18)	13.1	2
CH ₄	1303.6	3.8 (-18)	11.7	1
H ₂	4135.5	≥9 (-20)	≤42	3
HCO	1843.3	9.6 (-18)	0.6	4
c o	2135.1	1.1 (-17)	9.2	5
CO ₂	2341.9	7.6 (-17)	1.7	6
unid.	1192.1			
unid.	1161.9			
unid.	1090.7			
unid.	910.5			

* 1. Hudgins *et al.* (1993). 2. Schutte *et al.* (1993). 3. Sandford and Allamandola (1993). 4. Milligan and Jacox (1971). 5. Jiang *et al.* (1975). 6. Yamada and Person (1964).

charge lamp produces a flux of -2×10^{15} photons cm⁻² s⁻¹ ($E_{\text{ph}} \geq 6$ eV; Jenniskens *et al.*, 1993). For comparison, the UV flux inside dense clouds is estimated to be between 10^3 and 10^4 photons cm⁻² s⁻¹ (e.g. Schutte and Greenberg, 1991), implying that 1 min of irradiation in the laboratory corresponds to an equivalent processing of -4×10^5 – 4×10^6 years inside a dense interstellar region. The spectrum has been stretched in the Y-direction to display more clearly the relatively small peaks due to the photochemically produced species. Table 2 lists the positions of the new bands together with their identifications. Products are H₂CO, CH₄, H₂, CO₂, CO and HCO, consistent with the results of earlier studies of photochemistry of ices containing methanol (Allamandola *et al.*, 1988; Sandford and Allamandola, 1993). A few minor features appear which have not yet been identified.

Figure 2 shows the measured column density of the products as a function of irradiation time. The IR band strengths used to obtain these values were taken from the

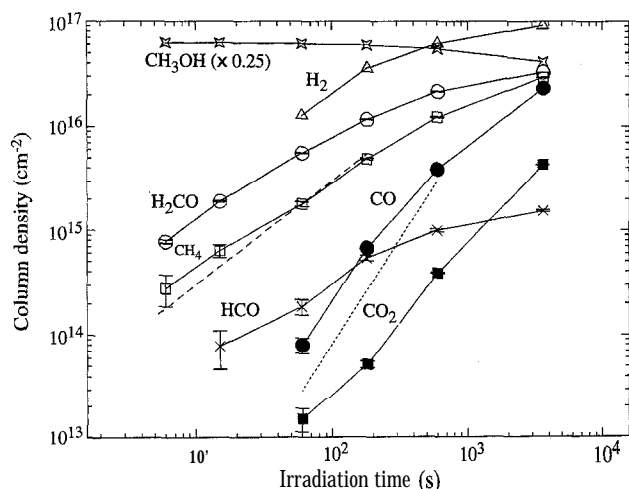


Fig. 2. Column density as a function of irradiation time for methanol and the photoproducts. The long dashed line gives a linear time dependence, the short dashed line gives a quadratic time dependence

literature (see Table 2). Except for the H₂ molecule, which is only IR active because of the matrix-induced perturbation of its transitions, band strengths were used as found for pure ices. We thus generalize our results for CO and CO₂, which indicated that band strengths are only weakly dependent on the ice environment. In the case of HCO, for which no band strengths are available, we assumed that the 1843 cm⁻¹ band has the same strength as the 1726 cm⁻¹ feature of H₂CO. The dashed and dotted lines in Fig. 2 trace linear and quadratic time dependencies, expected for first and second order photo-products, respectively. It can be seen that H₂CO, CH₄ and H₂ closely follow the linear dependence upon initial irradiation, suggesting that they are directly produced from photodissociation of methanol by splitting off H₂ or O. The initial time dependence of the HCO concentration is also nearly linear. Apparently one UV photon may be able to split off three hydrogen atoms at once, as is necessary for the direct formation of this radical. CO and CO₂ follow a steeper dependence, indicating these species to be higher order products of the photochemistry.

Table 2 gives the abundance of methanol and the various photolysis products after 1 h of UV irradiation. The calculated total amount of carbon in the residual methanol and the new products deviates by 2% from the amount originally deposited in the form of CH₃OH. This small discrepancy is likely caused by small errors in the applied band intensities (Table 2). Since 35% of the methanol has been destroyed by the photolysis, the 2% deviation indicates that the typical error in the band intensities is $\leq 10\%$. Such small errors could easily originate from factors such as the small variability of the band intensities inside different ice matrices (for example, see Table 1) or uncertainties in the literature values related to the measurement techniques. These may involve inaccuracy in the assumed density of the ice sample or in the determination of the composition when mixed ices are used (e.g. Hudgins *et al.*, 1993; Schutte *et al.*, 1993). The total amount of oxygen accounted for after photolysis is 92% of the original. This discrepancy appears to be too large to be exclusively due to inaccuracy in the band intensities of the paramount oxygen-bearing photolysis products, i.e. CO and H₂CO. It thus seems likely that oxygen-containing IR-inactive or very weakly active species are produced, i.e. O₂ and atomic oxygen. This is consistent with the production of CH₄ as a first order product of the photolysis, implying the loss of oxygen atoms from the methanol. Future experiments with thicker irradiated methanol ice samples are necessary to search for the very weak 1550 cm⁻¹ feature of solid O₂ (Ehrenfreund *et al.*, 1992).

Since methanol is observed at abundances of up to 10% in interstellar ices (Grim *et al.*, 1991; Allamandola *et al.*, 1992), understanding its photochemistry could be of importance for the study of the chemical evolution of the icy mantles. A consequence of our results is that photolysis of methanol ice would be a source of both H₂CO and CH₄. Both molecules have been tentatively detected in interstellar ices (Lacy *et al.*, 1991; Schutte *et al.*, 1995). Although either of these species could also be produced by other mechanisms, e.g. surface reactions (Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985), observations of their relative abundances, as well as of the presence of

other features characteristic of photoproducts (e.g. Grim et al., 1989), would be an important diagnostic of a possible photochemical origin.

Acknowledgements. This work has greatly benefited from the suggestions of an anonymous referee. Partial funding was received from NASA grant NGR 33-018-148.

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