PHOTODESORPTION FROM INTERSTELLAR DUST GRAINS*

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Abstract. An experiment to measure the photodesorption of physisorbed gases from a cold fused quartz substrate by near UV photons is described. The observed yield (mol photon^{-1}) is as large as 10^{-5}, a higher yield is likely in the vacuum UV. Included is a discussion of the photodesorption process and some applications to the interstellar medium. The observed yield is enough to maintain molecular abundances in moderate density interstellar clouds in equilibrium.

1. Introduction

The abundance of molecules in the interstellar gas depends not only on the rates of the chemical reactions responsible for their formation and destruction but also on the equilibrium between adsorption onto and desorption from the surfaces of dust grains. Thermal evaporation times are extremely long at the very low temperatures typical of interstellar grains; at 15 K, a rather weakly adsorbed molecule, with $\Delta H_{ads}/R = 1000$ K, doesn't evaporate in the lifetime of the universe. The 'average' unshielded interstellar photon flux**, $\phi_p \sim 2 \times 10^8$ cm^{-2} s^{-1} ($\lambda < 400$ nm), bombards each adsorption site on a grain surface with one photon every 2.5×10^6 s. If photodesorption occurs with any appreciable efficiency then it is the dominant evaporation mechanism from grain surfaces (Watson and Salpeter, 1972a). This paper gives the results of an experiment to determine the quantum efficiency for photodesorption.

Photodesorption has received little study either experimentally or theoretically, even though it was reported nearly forty years ago (Terenin and Solonitzin 1959). Most of the published experimental work[†] has been on the desorption of chemisorbed O and CO from metals and semiconductors; almost no work has been reported on physisorbed species or at low temperatures.

Harrison and Schoen (1967) have proposed the erosion of ice particles in Saturn's rings by photodesorption.[‡] Watson and Salpeter (1972a, b) have recently argued for efficient photodesorption by 100–200 nm photons and then calculated molecular abundances in the interstellar gas on that basis.

** The radiation field adopted is that of Werner and Salpeter (1969).
[†] See most recently: Lee (1972), Menzel *et al.* (1971), Baidyaroy *et al.* (1971), Peavey and Lichtman (1971), and Genequand (1971), and references contained therein. The most relevant experiment was never published (Reeves *et al.*, 1966).
[‡] The word photodesorption will be used to cover all photon induced processes which remove the first layer of atoms or molecules from a surface by nonthermal mechanisms. Many other terms are used, e.g.: photoejection, photosputtering, photoevaporation, optical erosion, photon induced desorption, photodetachment, etc.

2. The Experiment

A typical experiment to observe photodesorption consists of an adsorption substrate in a vacuum chamber, a source of illumination and a detector for measuring the increase in pressure caused by the additional gas desorbed under irradiation. The major difficulty in making quantitative studies is separating the true photodesorption from thermal desorption due to radiant heating of the sample and chamber by the large photon fluxes required for measurable pressure increases. Various means have been used in previous experiments to rule out thermal effects, with success that is in dispute (Genequand, 1971; Schubert and Böer, 1971). The design of the present experiment involved three stratagems to reduce thermal interference: the sample chamber and substrate were made of fused quartz in order to be transparent to the radiation; the radiation was chopped at a high rate compared to thermal time constants; finally the spectral dependence of the desorption signal was observed.

The vacuum system was a bakeable (700 K) uhv system made of pyrex, quartz and metal, pumped by a combination of a Hg-diffusion pump (with two re-entrant liquid nitrogen traps) and a titanium getter pump; residual pressure was typically $< 2 \times 10^{-10}$ torr (1 torr = 1.333×10^2 N m^{-2}). Sample gases were admitted with a metal seal variable leak valve at pressures between $1 - 100 \times 10^{-9}$ torr. The adsorption substrate was cooled with liquid nitrogen although some desorption was seen at room temperature. Depending on the vapor pressure of the sample gas at 77 K, the pressure during measurements was either the residual pressure or maintained near 1×10^{-8} torr.

The light source was a 1000 W Hg–Xe high pressure arc lamp and the beam was mechanically chopped at 37 Hz. The optics formed an image of the arc of approximate area 3 cm^2 on the substrate. The lamp output was filtered through a water cell (no photodesorption signal was observed between the water cutoff at $\sim$ 1000 nm and the

TABLE I

Photodesorption yield

$$\text{Yield} \equiv \frac{\text{molecules out}}{\text{photons in}}$$

Y	Molecule	Comment
$\sim 1 \times 10^{-5}$	CS_2	abs. 290–400 nm, < 220 nm
$\sim 1 \times 10^{-6}$	CO_2	no abs. > 175 nm
	$O_2(O_4?)$	only forbidden abs. > 200 nm, $\theta < 1$
	CO	only forbidden abs. > 200 nm, $\theta < 1$
10^{-7}–10^{-6}	C_6H_6	abs. near 260 nm
	C_4H_{10}	
	N_2	$\theta < 1$
	CH_4	$\theta < 1$, no absorption
	H_2O	only first layer desorbed, no absorption
	CH_3OH	only first layer desorbed
	NH_3	only first layer desorbed
$< 10^{-8}$	Cu_2O	experiment by M. Johnson, strong absorption < 250 nm
	CdS	experiment by M. Johnson, strong absorption < 310 nm

quartz cutoff at ~ 3000 nm, but this region was not carefully studied) and spectral regions could be isolated by a series of nested long-wavelength-pass filters. The desorption efficiences in Table I below are for the wavelength interval between the short wavelength cuton of the arc-quartz combination (~ 200 nm) and the cuton of a Schott WG-280 filter (~275 nm). The illumination of the entire cooled substrate in this band was measured calorimetrically to be 160 mW (2×10^{17} photons s^{-1}); the total power between the lamp cuton and the cutoff of the water cell was approximately 2 W. If the entire 2 W, modulated at 37 Hz, were absorbed at the surface of the quartz, then the temperature modulation at the chopping frequency would be 0.2 K. The true 'ac' temperature is much less than this because the quartz is transparent to the radiation, which has already been filtered through many thermal wave relaxation lengths of quartz.

The pressure was measured with a Varian UHV-12 Bayard-Alpert type ionization gauge; no calibration was made for the gases used which will introduce absolute errors of approximately a factor of two. The collector current was put into a fast feedback FET electrometer and then into a lock-in amplifier, whose d.c. output represents the pressure fluctuations, $| P_{ac} |$, synchronous with the chopped photon flux. In the case of CS_2, the large signal permitted direct observation of the time evolution of the pressure signal when the electrometer output was put into a signal averaging computer. By using short pulses of light (pressure bursts), the vacuum system response was determined; by using very long pulses, a further indication was available that the signal was photodesorption, rather than thermally induced desorption.

The use of an ion gauge to measure the pressure has a major drawback in that one cannot identify the chemical species responsible for the signal. Therefore, in the present experiment one cannot completely exclude the possibility of either contamination (which can partly be ruled out by sample techniques, wavelength dependence, consistency and other experimental variables) or chemical reactions (Moesta and Trappen, 1970). A mass spectrometer can be used but suffers from shot noise ~ 100 times worse than an ion gauge (Redhead *et al.*, 1968). The shot noise with an ion gauge at a dc pressure of 3×10^{-9} torr is 10^{-13} torr $Hz^{-\frac{1}{2}}$ allowing a useful sensitivity of a ~ 10^{-14} torr.

The response of the vacuum system is governed by the differential equation

$$V \frac{dP}{dt} = -SP + Q,$$

where V is the volume, P the pressure, S the pumping speed (customary unit, s^{-1}) and Q the gas throughput (customary unit, torr l s^{-1} = 3.536×10^{19} mol s^{-1}). Q in this case is due to outgassing, responsible for the residual pressure; thermal desorption due to slow heating of the substrate; and the photodesorbed gas $Q'e^{-i\omega t}$, where $\omega =$ (2π) × (chopping frequency). The expression for the pressure modulation synchronous with the chopped light (with the appropriate phase shift) is

$$| P_{ac} | = \frac{Q'}{V}(\tau^{-2} + \omega^2)^{-\frac{1}{2}},$$

where $\tau = V/S = 5.4$ ms, $\omega = 232$ rad s^{-1} and $V \cong 500$ cm^3, yielding

$$Q' = 5.3 \times 10^{21} \left(\frac{P_{ac}}{1 \, \text{torr}}\right) \text{mol s}^{-1}.$$

Typical signal levels were of the magnitude $P_{ac} = 10^{-11}$ torr or $\sim 10^{11}$ mol s^{-1}. No nonlinearity of signal intensity with changes in light intensity was observed.

3. Results

Table I presents the major results of this investigation. The quantity Y is the yield, the number of molecules desorbed per photon incident ($\lambda < 275$ nm). It is quoted only to an order of magnitude for the various gases because systematic errors such as calibration, contamination, and in some cases, thermal desorption, are not totally eliminated. For CS_2, which received the most study, the error is more likely to be less than a factor of three. Some of the gases with low adsorption energies do not adsorb a complete monolayer (the degree of coverage, θ, is less than 1) at 77 K, and it is hard to estimate θ accurately, but it cannot be very low judging by the signal levels.

Desorption was observed for a number of materials which show little or no uv absorption in this region when in the gaseous state. This is consistent with previous studies (Moesta and Trappen, 1970; Hubbard et al., 1971; Breuer, 1973) which have observed efficient photocatalysis on surfaces with photons of longer wavelength than are capable of gas phase photolysis. The spectral dependences of the photodesorption yields have not been carefully analyzed although certain features are obvious in the data: that the desorption yield falls off markedly with increasing λ, but that some desorption does persist through most of the visible region for some gases. No sharp features were observed with the available resolution of ~ 10 nm in the integrated spectra taken with the nested filter set. The spectra have different shapes for the various molecules, as is expected of true photodesorption.

The values of Y may seem to be small at first glance, but one must realize that only photons that are absorbed in the first monolayer (perhaps a few layers) are likely to lead to desorption. A quantity that is more revealing is the cross section for photodesorption, $\sigma_{PD} = Y\sigma_m/\theta$, where σ_m is the area of a molecule adsorbed on a surface (typically 2×10^{-15} cm^2) at monolayer coverage. A yield of 10^{-5} corresponds to a rather large cross section of $\sim 2 \times 10^{-20}$ cm^2 ($\theta = 1$).

One can also define the relative quantum efficiency $\eta = \sigma_{PD}/\sigma_{abs}$, where σ_{abs} is the cross section for absorption of photons by the adsorbed layer. One can express η in terms of macroscopic quantities

$$\eta = \frac{Y}{Kd},$$

where $K[\text{cm}^{-1}]$ is the attenuation coefficient and d is the thickness of the monolayer. The denominator is just the fractional number of photons, $F = \Delta I/I$, absorbed in passing through one layer. Photodesorption in wavelength regions for which the

sample gas is transparent excludes the use of the gas phase value for the attenuation coefficient in the calculation of η. At present one cannot calculate the absorption spectrum of the adsorbed layer, in fact, very little is known about the excited electronic states of adsorbed molecules. (Data is just becoming available on vibrational spectra, see for example Heidberg *et al.*, 1971.) Photodesorption is a useful technique for gaining this knowledge, due to its easily adjustable energy resolution and sensitivity to broad as well as narrow spectral features; presuming that we can understand the ejection mechanism well enough to decouple it from the absorption.

Let $f(\Delta v)$ be the total oscillator strength for all transitions of an adsorbed molecule in some extended wavelength region Δv. Surface phonons broaden out individual transitions, so that a monolayer is optically thin, even at a line center, i.e. $\sigma_{abs}(v) < \sigma_m$. The average absorption cross section is then

$$\bar{\sigma}_{abs} = \frac{1}{\Delta v} \int \sigma(v)\, dv = \frac{1}{\Delta v} \frac{\pi e^2}{mc} f(\Delta v)$$

and $F = \bar{\sigma}_{abs}/\sigma_m$. For the observed region $F = 3.2 \times 10^{-2} f(\Delta v)$. We might expect $f(\Delta v)$ to be of the order of 10^{-3} corresponding to a mean attenuation coefficient $K \sim 10^3$ cm^{-1}, but K could be as high as 10^5 cm^{-1} which is typical of vacuum UV absorptions in gases and direct band gap absorptions in solids.

If we provisionally adopt $f(\Delta v) = 10^{-3}$ for CS$_2$ then the observed yield of 10^{-5} implies that $\eta \sim \frac{1}{3}$, i.e. that a substantial fraction of the photons absorbed lead to desorption of a molecule. Of course a higher f value would lower η proportionately.

Water, ammonia and methanol gave moderate desorption yields for the first layer adsorbed on the quartz, but the next layer adsorbed on top was desorbed much less strongly, if at all. A variety of explanations are possible and the present data does not allow differentiation.

Also given in Table I are two unpublished results of a related experiment by Michael Johnson, also at Berkeley. Thin films ($\sim$ 30 nm thick) of the ionic materials CdS and Cu$_2$O were given prolonged intense uv bombardments, $> 3 \times 10^{24}$ photons cm^{-2} beyond the band gap energy, at the end of which no decrease in thickness was apparent. The upper limits set to the rate of photodesorption of these ionically bonded materials are consistent with the qualitative discussion by Dexter (1964).

4. Discussion

There are several major categories of ejection mechanisms that can be responsible for photodesorption.

(1) For chemisorbed species, the photon can break the bond to the surface, allowing desorption of a neutral molecule (atom) or an ion, possibly by subsequent thermal evaporation. Photodesorption and electron induced desorption of CO from metals is thought to occur this way (Menzel *et al.*, 1971).

(2) An adsorbed molecule can undergo photodissociation or photoionization, with desorption of the fragments.

(3) The adsorbed molecule makes a transition to an excited electronic state and is desorbed before it deexcites (Watson and Salpeter, 1972a).

(4) The molecule goes up to an excited electronic state, returns to the ground electronic state, but in an excited vibration-rotation level. Some of this internal kinetic energy is converted to translational energy away from the surface by collision with surface atoms.

(5) The bonds in the surface layer of the substrate are excited and lead to desorption either due to changes in the adsorption potential or transfer of the excitation as in 4.

Mechanism 1 can be ignored when discussing physisorbed molecules. Mechanism 2 is not likely with the low energy photons, $E < 6$ eV in this experiment. Mechanism 3 requires that the photon be of shorter wavelength than that absorbed by the gaseous molecule; it can be responsible for some but not all the observed desorption. Mechanism 5 is possible and may be responsible for some of the long wave ($\lambda > 400$ nm) desorption, which was similar in spectral shape for many of the molecules, but rapid diffusion of the excitation will inhibit this mechanism. Mechanism 4 is flexible enough to be possible whether the absorption is redshifted (i.e. the excited state is more tightly bound to the surface than the ground state, perhaps by chemical forces) or is blueshifted, with respect to the gaseous absorption. The high desorption yield for CS_2 which is linear in the ground state and bent in its excited states, may be an indication that Mechanism 4 is responsible, but this could just be a selection effect due to the wavelength dependence of σ_{abs}. All mechanisms except 4 can desorb single atoms as well as molecules.

5. Conclusions

The main conclusion is that photodesorption is an efficient process, with an efficiency, η, which may be as high as order unity. In spectral regions of high absorption, the photodesorption yield Y may be as high as 10^{-2} but even a yield of 10^{-6} cannot be neglected. In a region of moderately high density ($n_H + 2n_{H_2} = 10^3$ cm^{-3}, $n_O = 1$ cm^{-3}, $n_{mol} = 10^{-2}$ cm^{-3}, $T_{gas} = 50$ K) the flux of molecules, ϕ_m, is ~ 50 cm^{-2} s^{-1} which is down by a factor of 4×10^6 from the average unshielded interstellar radiation field. Thus, the photons can return molecules to the gas as fast as they collide with grains, preventing depletion of the gas, at least in regions of modest shielding. Photodesorption can likewise maintain an equilibrium abundance of $\sim 10^{-2}$ cm^{-3} in a dense completely molecular cloud (molecular formation has gone to completion). The column density of molecules through such a cloud is approximately $Y\phi_p L/\bar{v}$ where L is the mean free path of the photons and $\bar{v}$ is the mean velocity of the molecules and ϕ_p is the photon flux outside the cloud.

The equilibrium coverage of grain surfaces and the question of mantle growth depends not only on ϕ_m, but also on the rate of molecular formation on grain surfaces. If the fraction of molecules that remain on the surface during formation is δ, ϕ_a is the flux of heavy atoms and we assume (Watson and Salpeter, 1972a) that every heavy atom forms a molecule when it hits a grain, the criterion for mantle growth becomes $(\phi_m + \delta\phi_a) > Y\phi_p$. The conditions for which this is satisfied depends on the value of Y

and the amount of UV extinction. If δ is nearly 1, then the molecules we observe in the gas that were formed on grains were photodesorbed, except H_2 which can evaporate thermally. If photodesorption occurs by Mechanism 4, then it may indicate that δ is small, since molecules are probably formed in states of high vibrational and rotational excitation. Mantles that are formed in regions of high shielding, will be destroyed if the grain migrates to the surface of the cloud or if a star should form in the cloud. The interstellar flux ϕ_p with a yield of 10^{-5} will remove a 100 nm thick mantle in 10^6 yr, but the yield may be lower for ice mantles. In circumstellar regions, around newly formed stars, and in the solar system the photon flux is much higher but thermal evaporation also becomes important. Another interesting application occurs in circumstellar regions. The momentum transfer to the grain due to recoil when a molecule becomes photodesorbed is greater than the momentum of the photon if $Y > 10^{-4}$, so photodesorption increases the radiation pressure of uv photons.

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Photodesorption is an interesting and neglected process which certainly deserves further study which will contribute to both astrophysics and surface chemistry.

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