

Photodissociation

Ewine F. van Dishoeck

Leiden Observatory/MPE

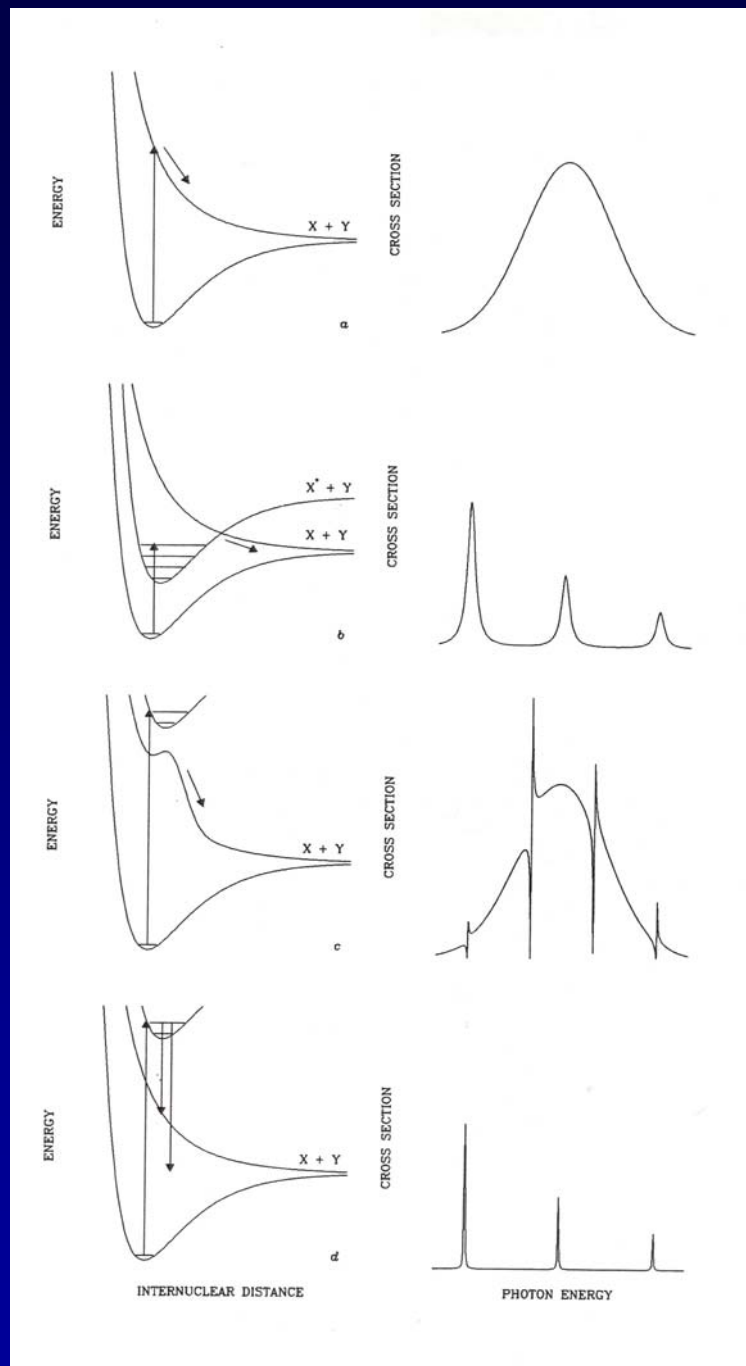
www.strw.leidenuniv.nl/~ewine/photo

**Based on reviews by van Dishoeck (1988), Kirby & van Dishoeck (1988),
Roberge et al. (1991), van Dishoeck et al. (2006),
van Hemert & van Dishoeck (2008)**

Overview

- **Processes**
- **Radiation fields of astrophysical interests**
- **Theory vs. experiments**
- **Small molecules**
- **Large molecules: PAHs**
- **Water ice**
- **Conclusions and questions**

Processes: small molecules



Direct p.d.

Ex: H_2^+ , OH, H_2O

Predissociation

Ex: CO

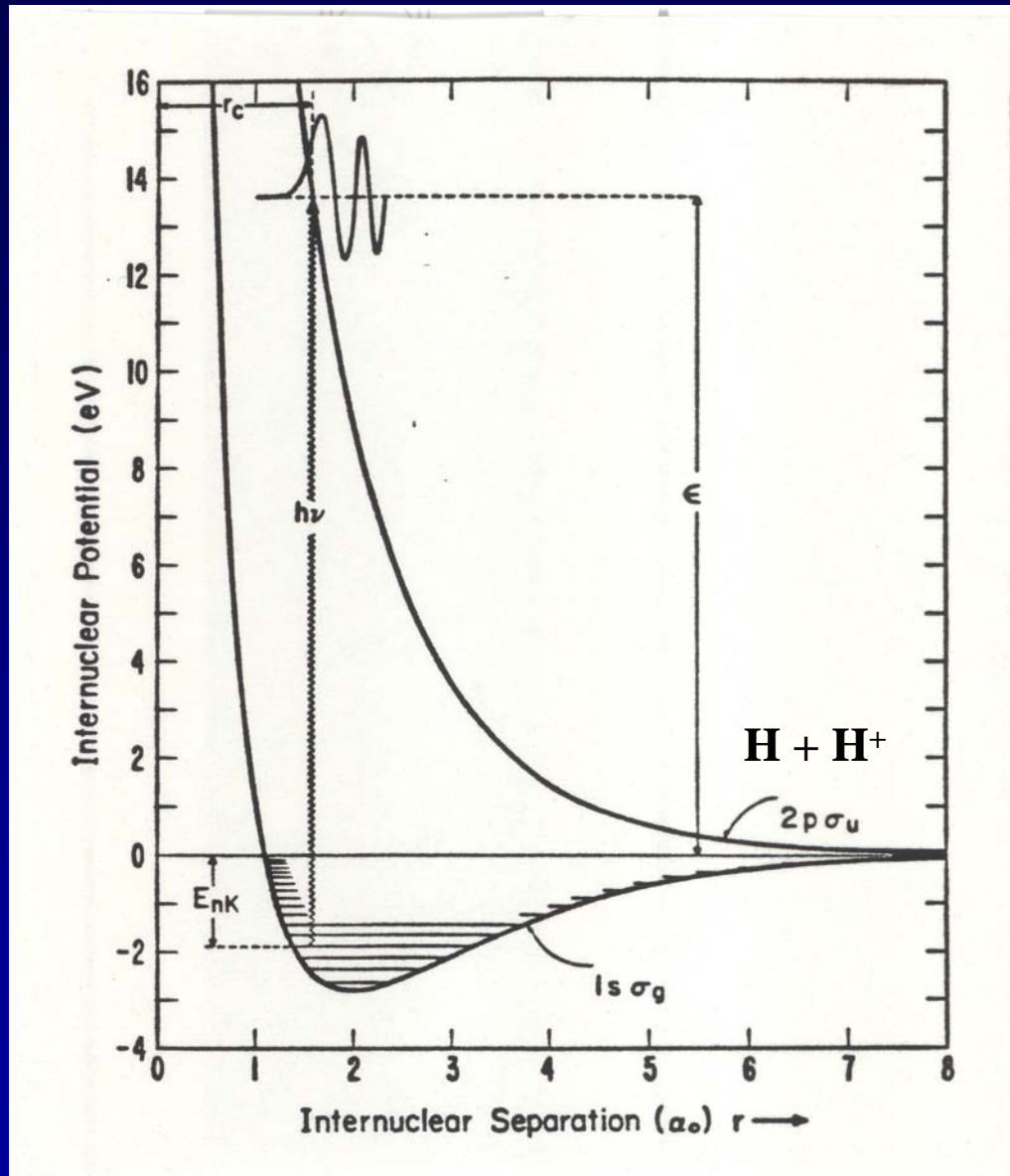
Coupled states p.d.

Ex: OH

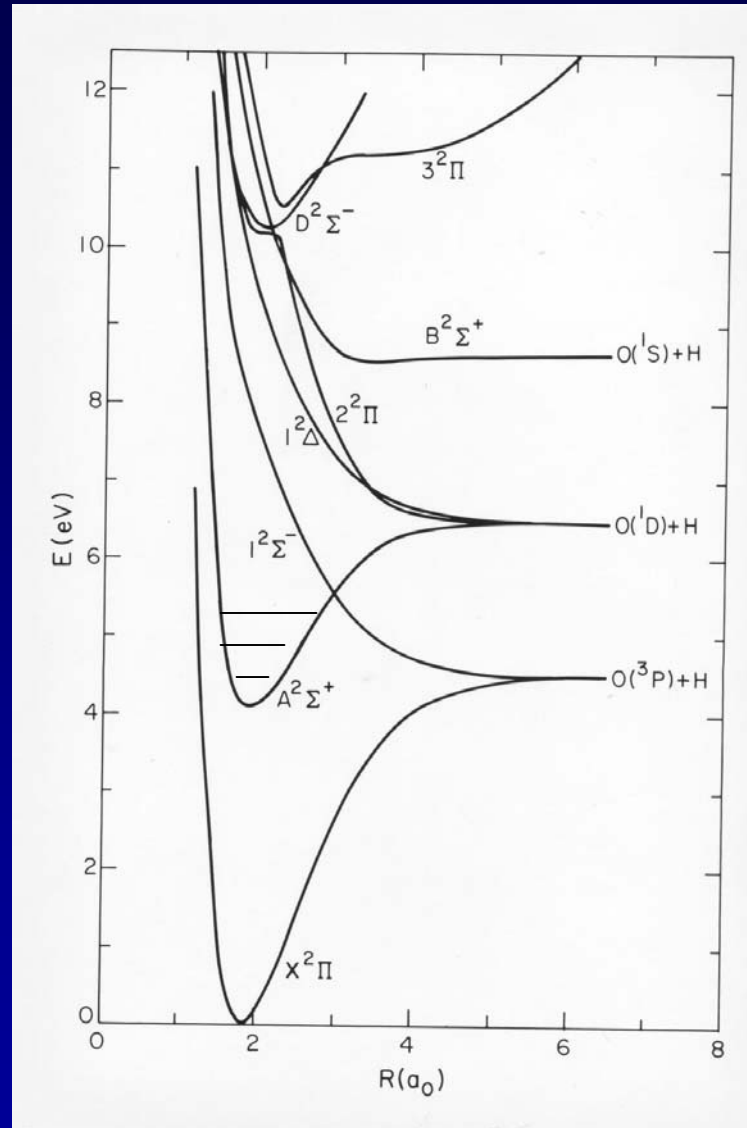
**Spontaneous
Radiative
dissociation**

Ex: H_2

Potential curves for H_2^+ ion



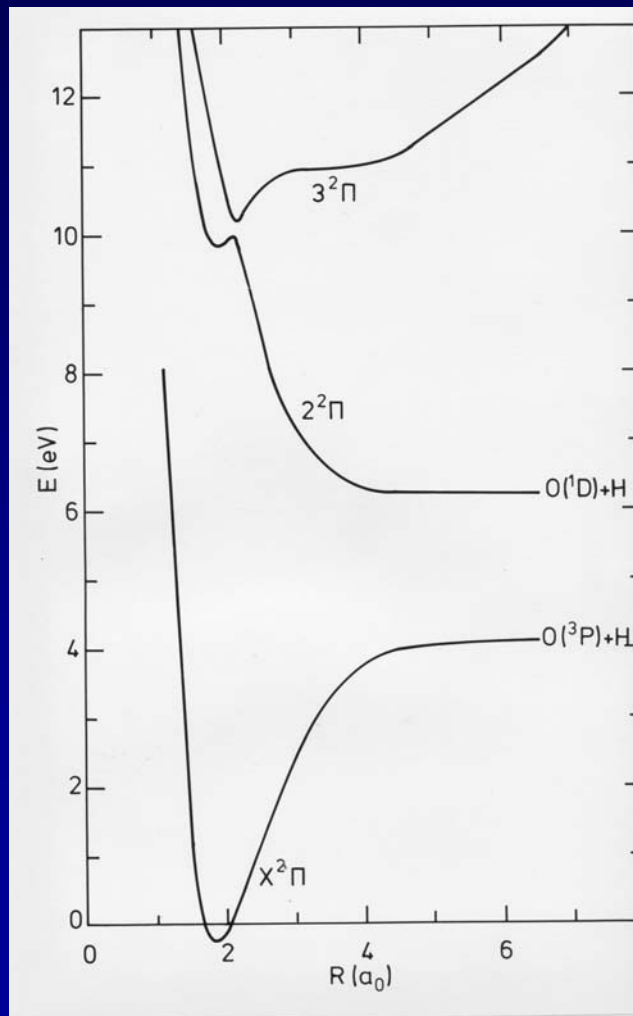
Potential curves OH



- All 4 processes contribute

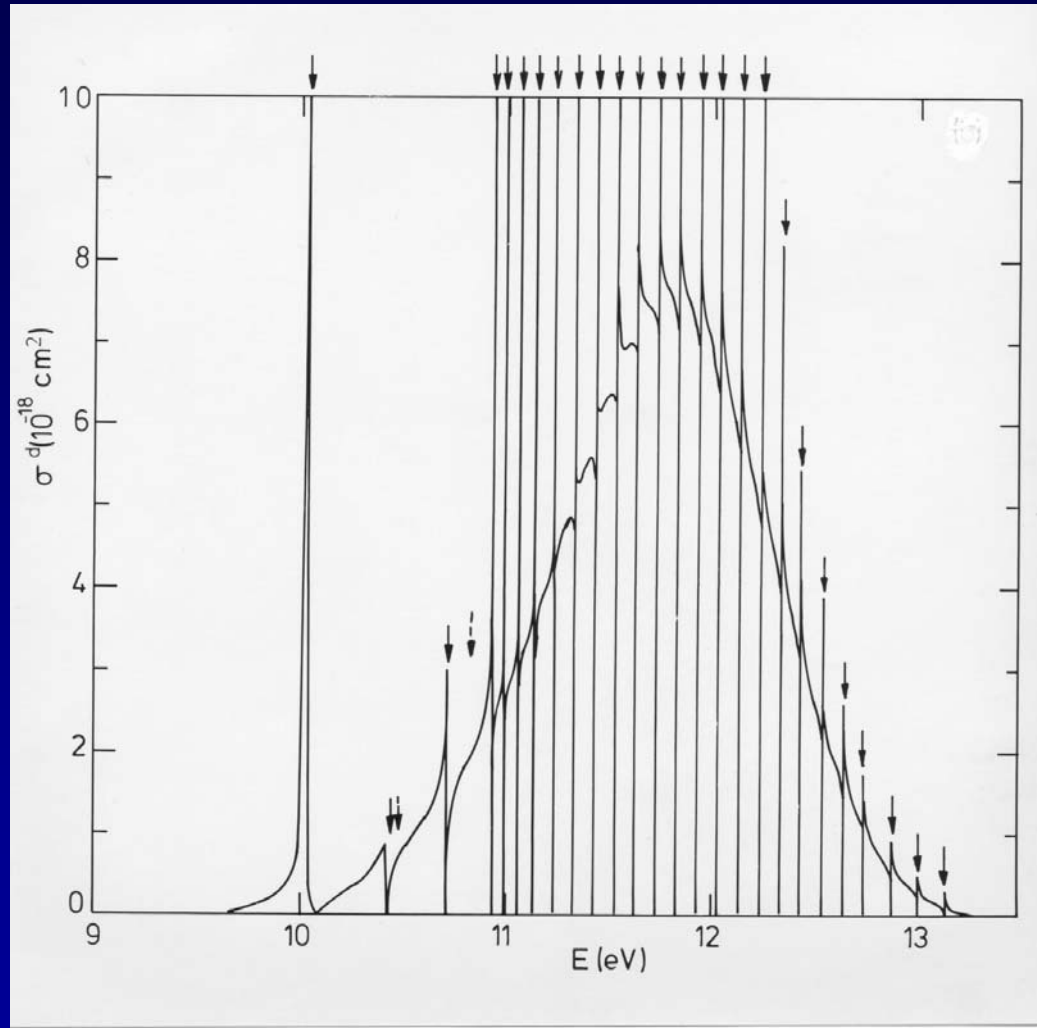
Photodissociation through coupled states

Non-adiabatic interactions in OH $2,3 \ ^2\Pi - X \ ^2\Pi$



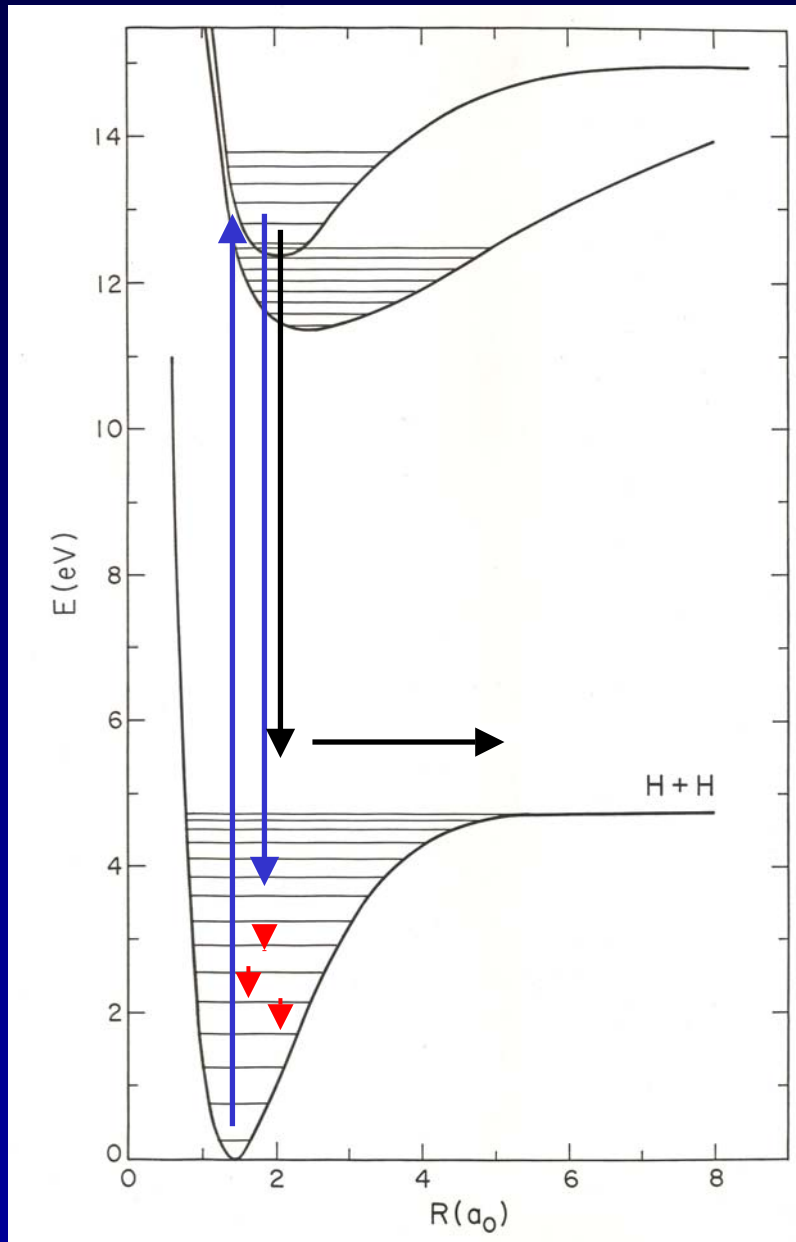
vD, vH, Alison & Dalgarno 1984

Solution of coupled equations



Resonances with Fano profiles, located close to vibrational levels in diabatic bound potential

H₂ spontaneous radiative dissociation



- 90% of absorptions into B and C states are followed by emission back into bound vibrational levels of the X state
- 10% of the absorptions are followed by emission into the unbound vibrational continuum, leading to dissociation

Photodissociation rate

- Continuum photodissociation

$$k_{pd} = \int_{912\text{\AA}}^{\infty} \sigma_{pd}(\lambda) I(\lambda) d\lambda$$

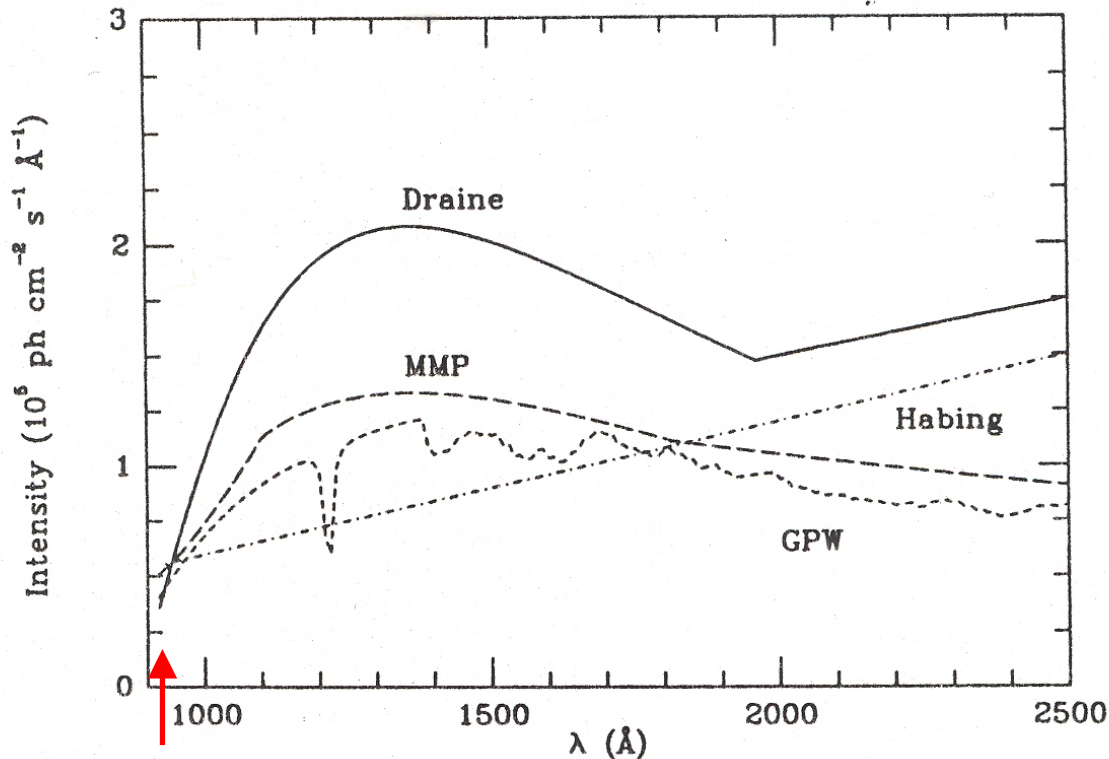
where σ_{pd} is the cross section in cm^2

- Discrete photodissociation

$$k_{pd} = \sum_{\text{lines}} \frac{\pi e^2}{m_e c^2} \lambda_{\text{line}}^2 f_{\text{line}} \eta_{\text{line}} I(\lambda_{\text{line}})$$

where f is oscillator strength and η is the dissociation probability

Interstellar radiation field

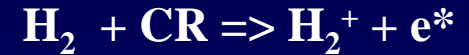
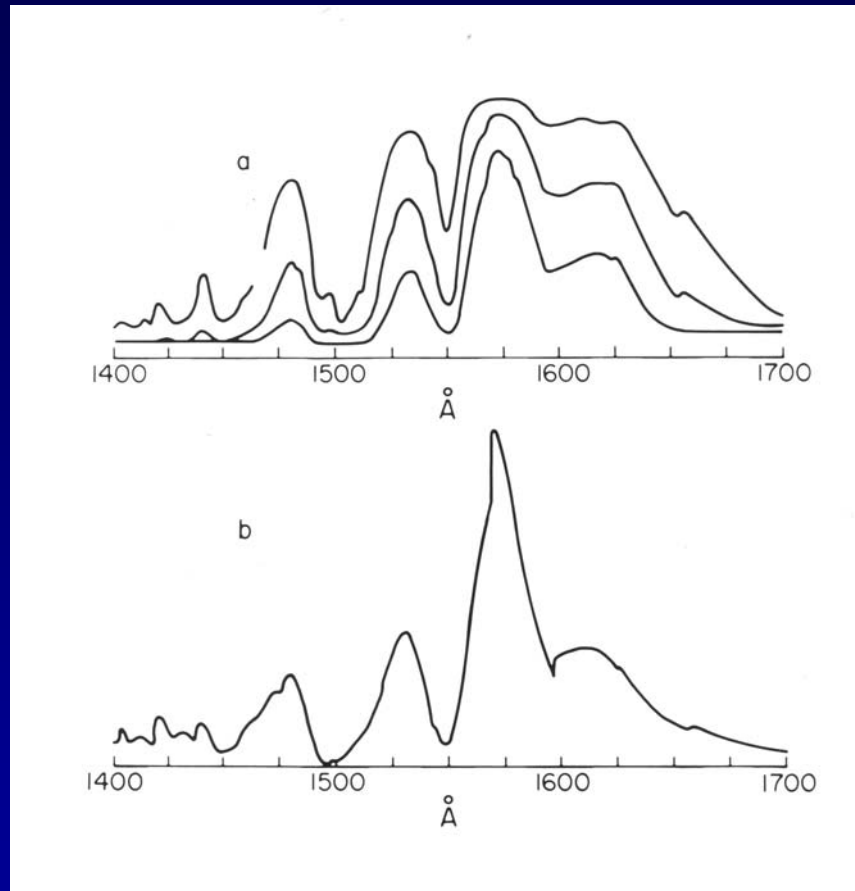


912 \AA = 13.6 eV cutoff

Figure 5. The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long-dashed line), Gondhalekar et al. (1980) (short-dashed line) and Habing (1968) (dash-dotted line).

Note linear scale; uncertainties $\sim 50\%$

Cosmic-ray induced radiation



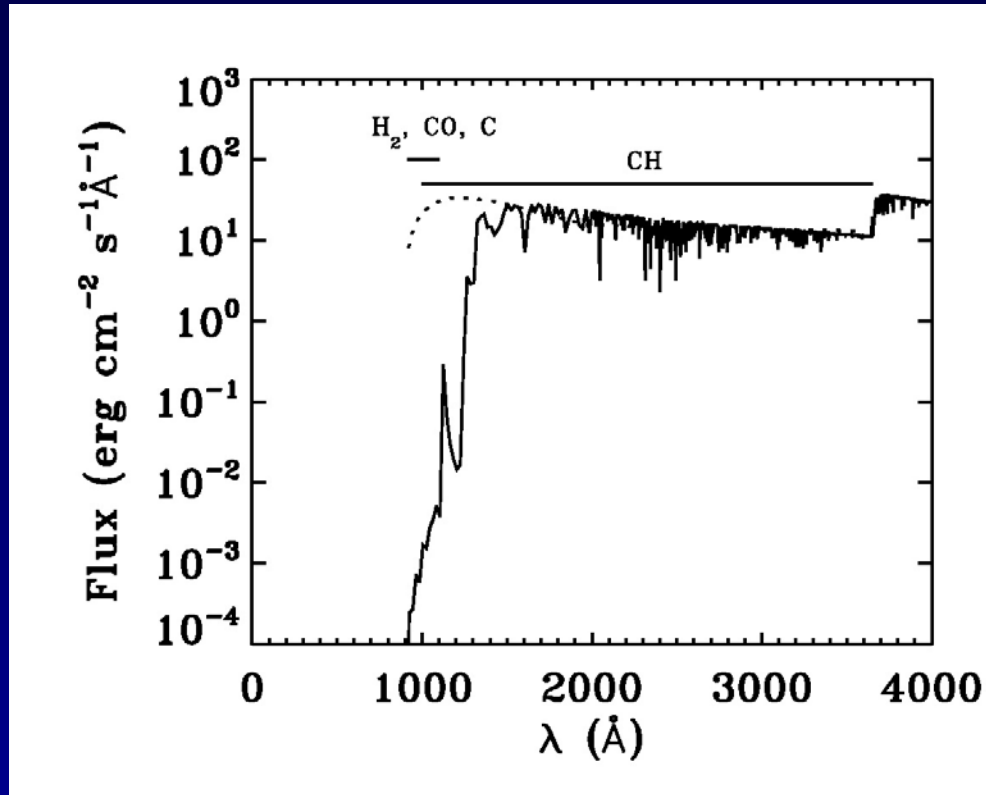
Stephens & Dalgarno 1970
Gredel et al. 1987

-Detailed line + continuum spectrum peaking around 1600 Å and continuing below 912 Å

Other radiation fields

- Ly- α dominated
 - Shocks,
- Stellar blackbodies $T_{\text{eff}}=4000-10000$ K
 - Disks, cool PDRs, ...
- Solar radiation $T_{\text{eff}}=5500$ K + Ly α
 - Comets

A0 star radiation field vs. scaled ISRF



- Results sensitive to adopted UV field, especially $<1100 \text{\AA}$
- Affects some molecules, but not all

Attenuation of radiation in clouds

- Inside an interstellar cloud, $I(\lambda)$ will be diminished by several effects
- Continuum attenuation by dust grains: calculation depends on scattering properties of grains such as albedo and scattering phase function

$$I(A_V) \approx I_0(A_V = 0) \exp(-\gamma A_V)$$

↑
Intensity inside
cloud

↑
Intensity at
edge

↑
Depends on λ ,
grain properties: drops from 3
to 0.6 for μm size grains

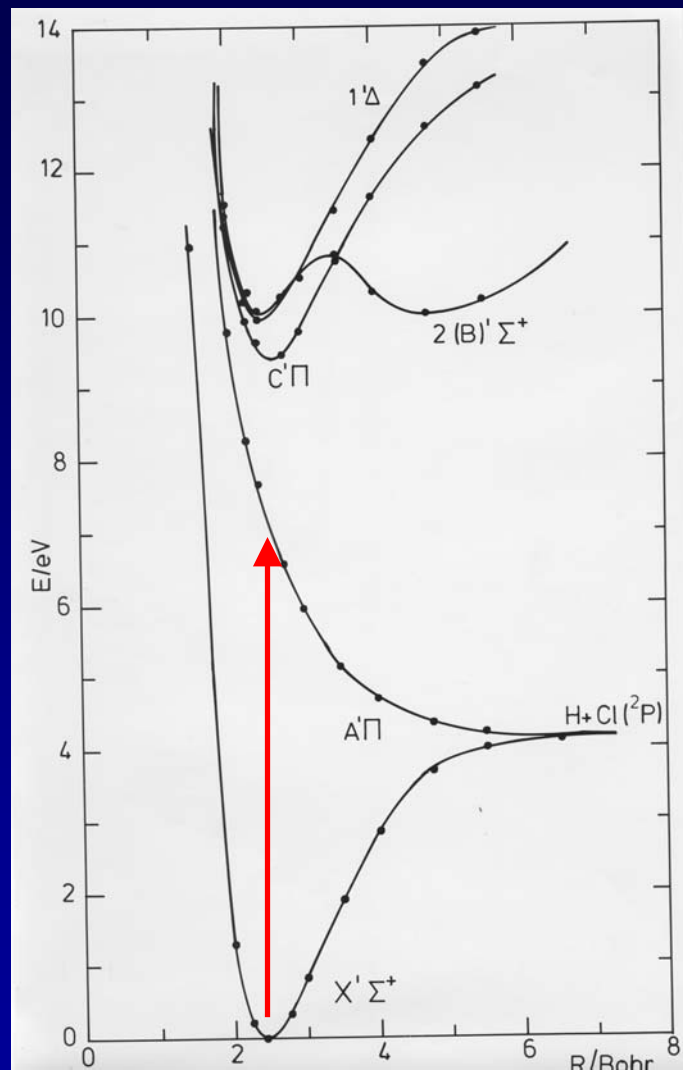
Cross sections: theory

- **Diatomics:**
 - **Ab initio quantum chemical calculation of potential curves and transition dipole moments for lowest ~5 roots of each symmetry**
 - **Solve for nuclear motion on surfaces, taking couplings between states into account**
 - **Compute cross sections by integration of product vibrational wave functions of ground and excited states and transition dipole moment.**

Works well if number of electrons not too large: ~30

Most hydrides of astrophysical interest calculated, some heavier diatomics

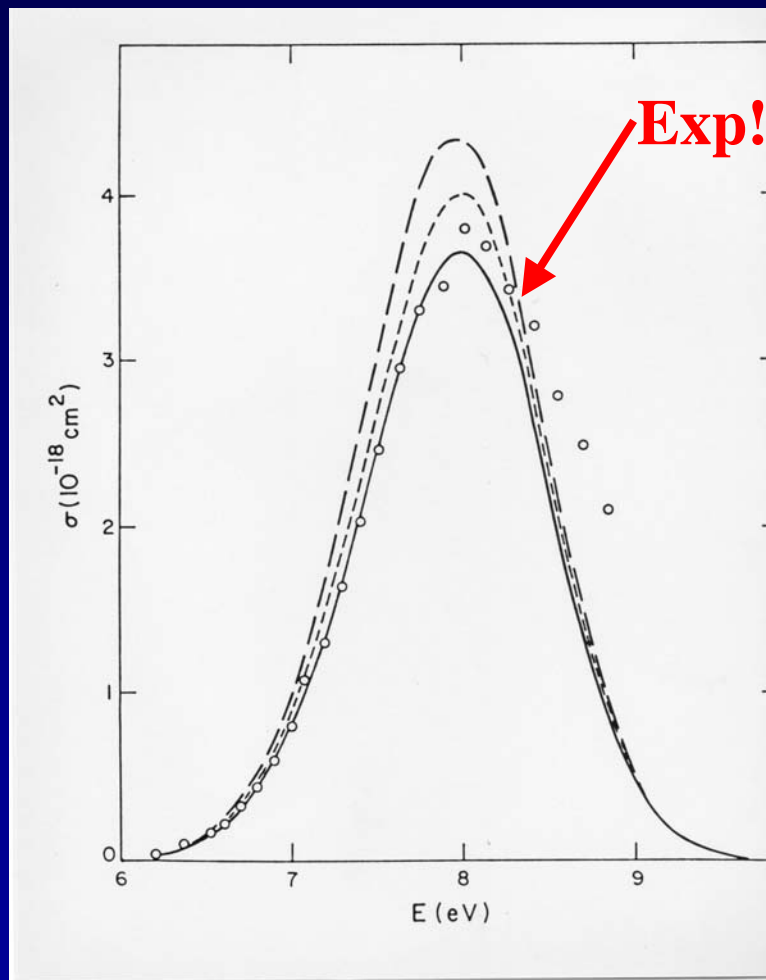
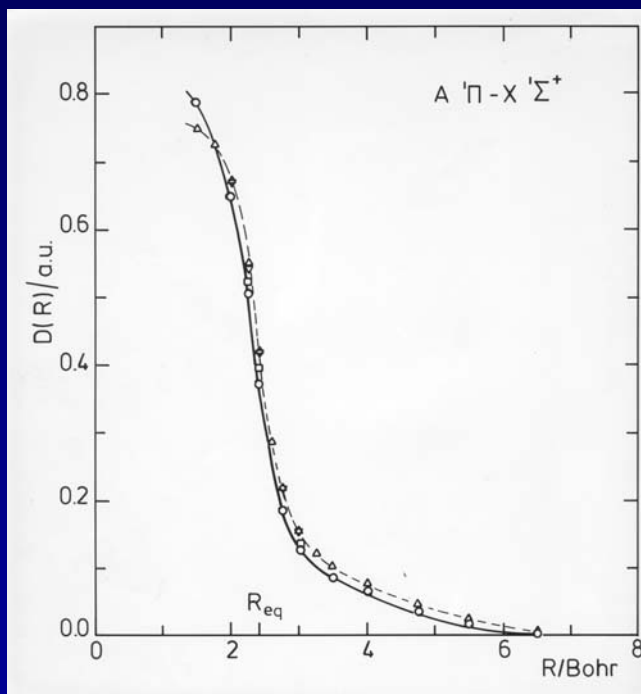
HCl as a test case



Quantitative comparison with experiment

HCl cross section A-X

Transition dipole moment function



- Excitation energies within 0.2-0.3 eV
- Oscillator strengths and cross sections within 20-30%

Cross sections: theory

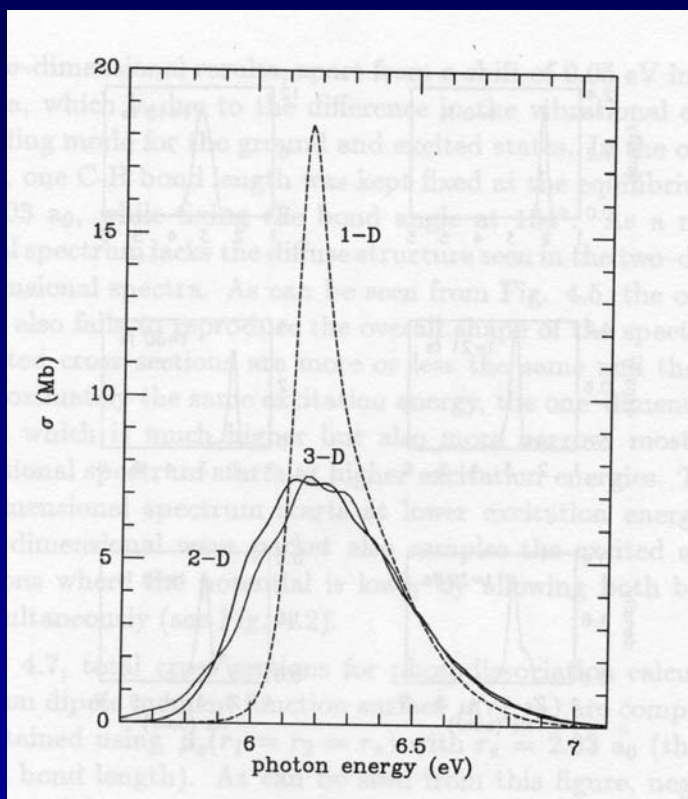
- **Triatomics**
 - Same recipe possible for light hydrides, but now calculating full 3D surfaces and solving dynamics in 3D
 - Excellent quantitative agreement with experiment for $\text{H}_2\text{O } \tilde{\text{A}} - \text{X}$ and higher transitions
 - Detailed predictions of product energy distributions, e.g., OH rotational excitation
 - Similar calculations for CH_2 , NH_2 , HCO^+
 - Very difficult for heavier triatomics
 - Ions, especially O-containing ones, lower rates

Kroes et al. 1993; Harreveld & van Hemert 2000-200x

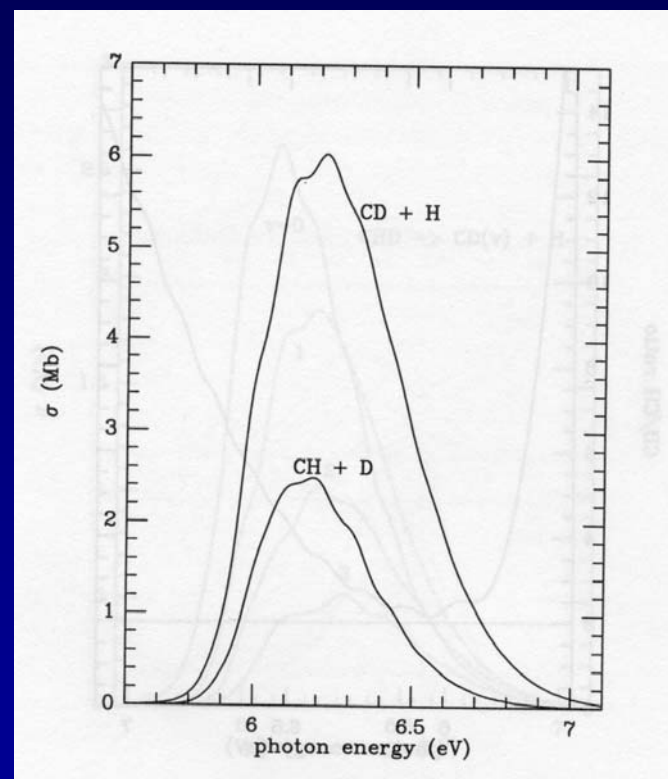
Bearda et al. 1994, vD et al. 1996, Vetter et al. 199x, Koch et al. 1995

Time-dependent wavepacket dynamics

From 1D => 3D



CD vs CH



Also: branching ratio to $C + H_2$ vs $CH + H$

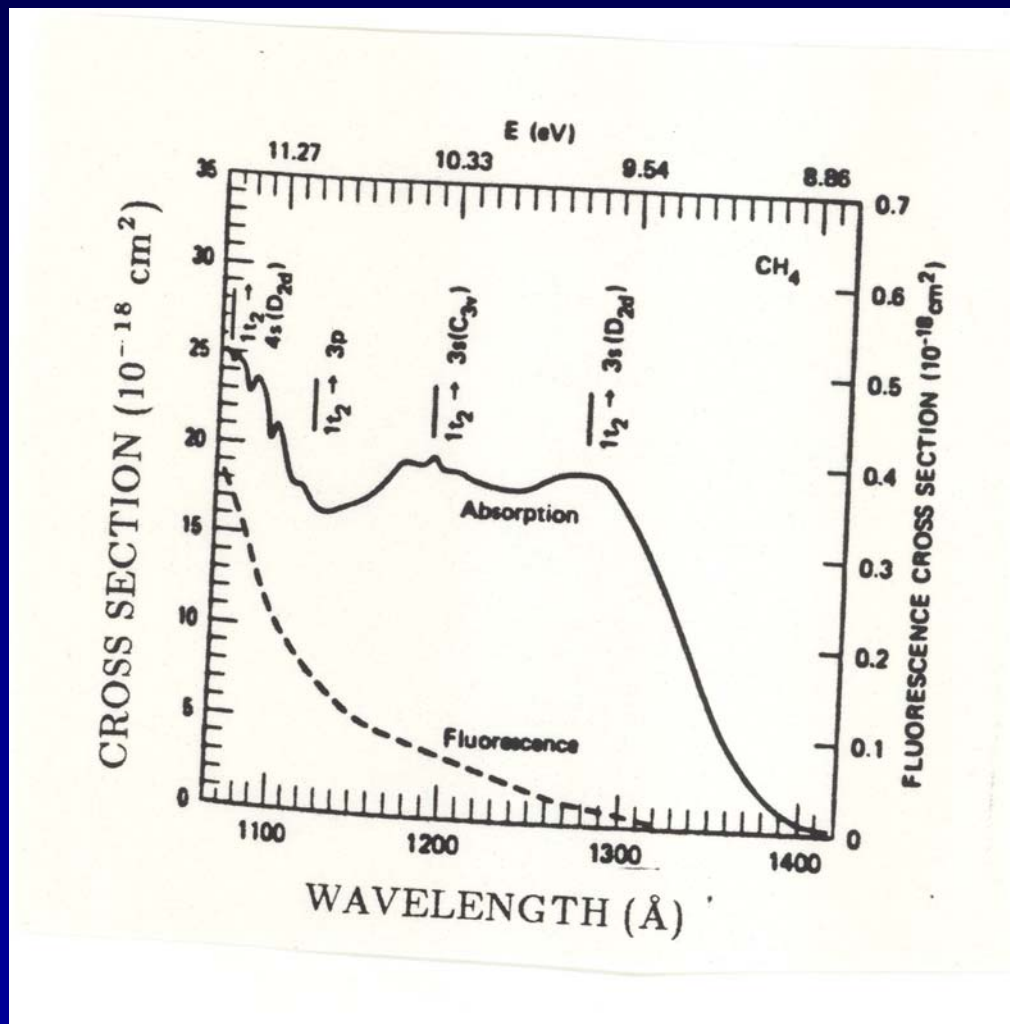
Cross sections: theory

- **Polyatomics**
 - **Only vertical excitation energies + transition dipole moments feasible**
 - **Use correlation diagrams to obtain insight whether dissociation likely**
 - **Simplest assumption: all transitions into states above E_{dis} and below E_{ion} lead to dissociation \Rightarrow *upper* limit to p.d. rate**

Cross sections: experiments

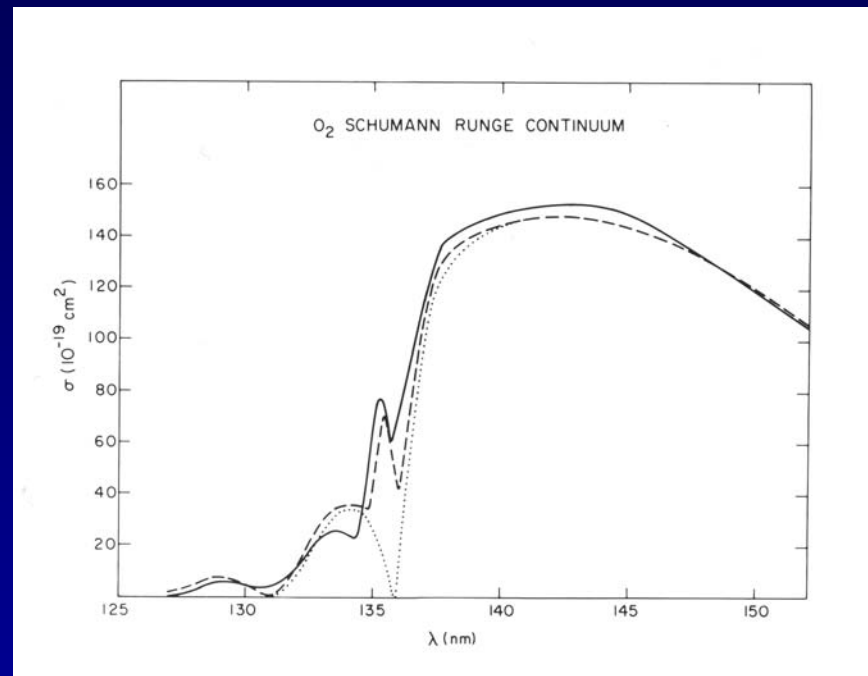
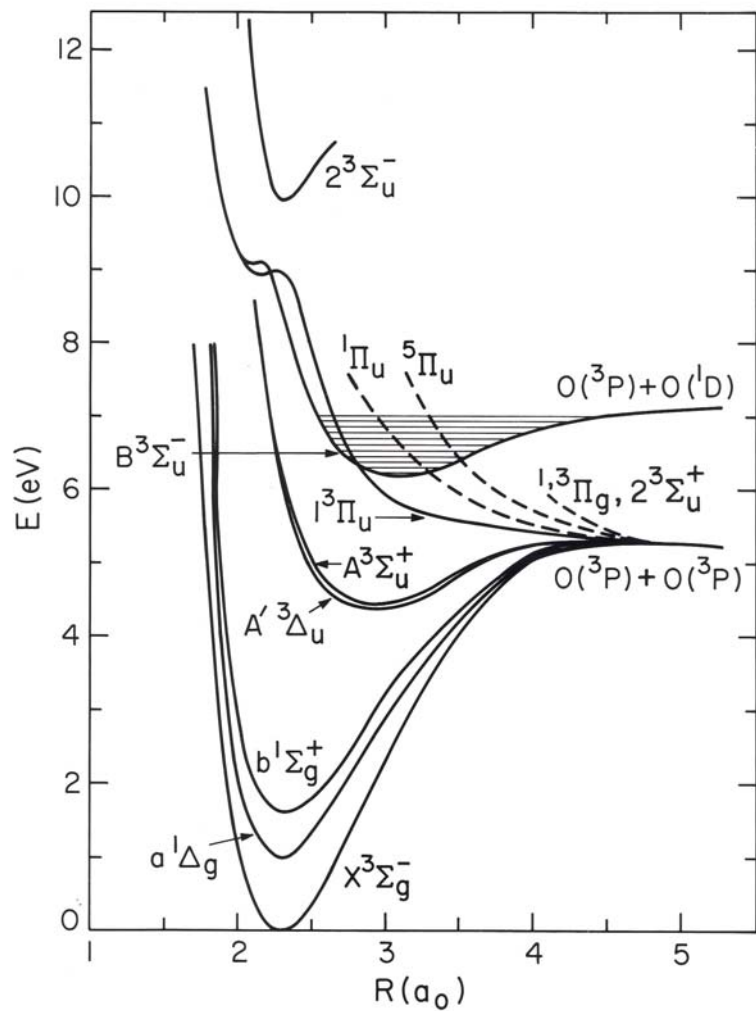
- **Limited (mostly) to stable molecules**
- **Absorption cross sections of many (stable) molecules measured over broad energy**
 - **High accuracy (~20%) if absorption is continuous**
 - **Large uncertainties (~order of magnitude) if absorption is discrete and lines unresolved**
- **Need to measure fluorescence and ionization cross sections to determine dissociation cross sections**
 - **Usually assume all absorptions above IP lead to ionization**

Example: CH₄



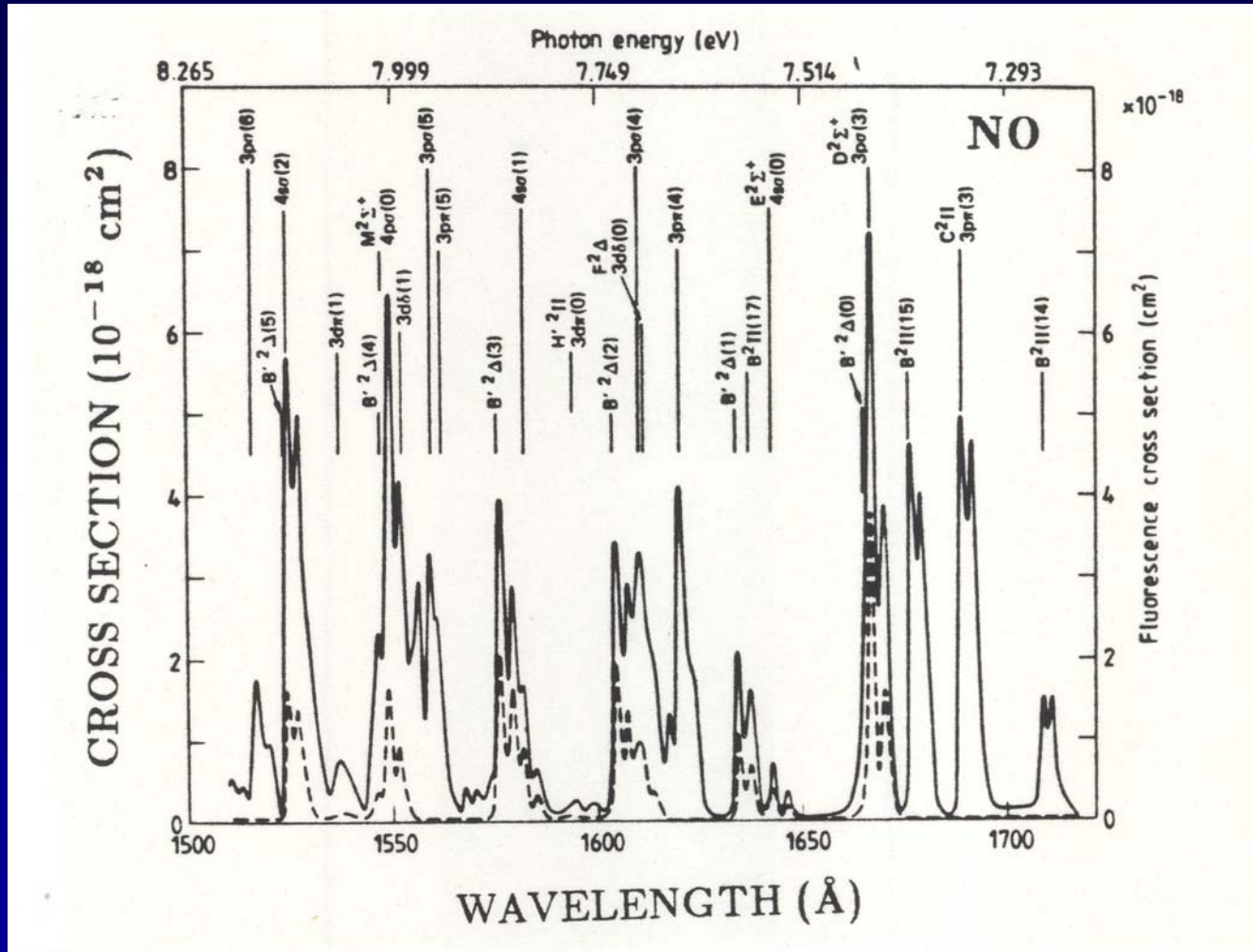
High accuracy

Example: O₂



High accuracy

Example: NO



Many unresolved bands => large uncertainties

Guest & Lee 1981

Cross sections: recent experiments

- Lots of beautiful experiments on state- and time-resolved photodissociation dynamics, but usually at a single wavelength (193 nm, 157 nm)
- Not much useful for astrophysics since 1980's
- CO measurements Eidelsberg, Rostas et al. => update of CO isotopic photodissociation in progress

Products

- **Diatomics: computed from dynamics, but outcome of predissociation process not well known if multiple states involved**
 - $\text{OH} \Rightarrow \text{O}(^3\text{P}), \text{O}(^1\text{D}), \text{O}(^1\text{S})$
 - $\text{CH}^+ \Rightarrow \text{C} + \text{H}^+$
 - Product ratio varies depending on radiation field
- **Triatomics: computed from dynamics for light hydrides, but only accurate for lowest states**
- **Polyatomics: unknown, both from theory and experiments; no reasonable guesses, except which products are energetically feasible**
 - What does UMIST06 assume?
 - Watch out for experiments at high pressure \Rightarrow subsequent reactions

Uncertainties

- **Rates: estimated by EvD based on above considerations and critical evaluation of literature; categories A (<50%), B (factor 2) or C (factor of 10)**
 - Includes estimates of higher-lying channels below IP or below 13.6 eV
 - Note: these assignments only hold for standard ISRF! Could be different for solar radiation field
- **Products: no quantification of uncertainties possible, except for simplest diatomics**

Photodissociation database

- Summarized in reviews and made available on WWW at www.strw.leidenuniv.nl/~ewine/photo
 - 71 molecules photodissociation
 - 21 atoms photoionization
 - 17 molecules photoionization
- Includes cross section files and rates for different radiation fields
- Comparison with Huebner et al. AMOP database in progress
- Direct integration of cross sections over radiation field and radiative transfer included in Leiden PDR code since mid-1990's (Jansen et al. 1995, van Zadelhoff et al. 2003, Jonkheid et al. 2004-2007)

Small carbonaceous molecules

- Use increased computing power to determine vertical excitation energies and oscillator strengths of 9 states per symmetry of heavier species
- C_3 , C_4 , C_2H , *l*- and *c*- C_3H , *l*- and *c*- C_3H_2 , HC_3H , *l*- C_4H and *l*- C_5H
- Compute E_{dis} and IP
- Assume all absorptions above E_{dis} and below IP lead to dissociation

Caveats

- Comparison with exp and other calculations shows that E_{ex} accurate to 0.2-0.3 eV and f to better than 30% for lower states
- Higher states (≥ 5 'th root per symmetry) difficult to calculate because of heavy mixing of states and orbitals
 - E_{ex} O.K. to determine whether below IP or 13.6 eV
 - Magnitude of f (strong, weak) O.K.
 - Several new, strong Rydberg states found
- Rates are upper limits (but expected to be close to actual values)

Photodissociation rates in ISRF

Species	Rate (s^{-1})
<i>l</i> -C ₃	5.0(-9)
<i>l</i> -C ₄	8.5(-9)
<i>l</i> -C ₂ H	1.6(-9)
<i>l</i> -C ₃ H	1.8(-9)
<i>c</i> -C ₃ H	1.1(-9)
<i>l</i> -C ₄ H	3.7(-9)
<i>l</i> -C ₅ H	1.3(-9)
HC ₃ H	2.2(-9)
<i>c</i> -C ₃ H ₂	1.4(-9)
<i>l</i> -C ₃ H ₂	5.1(-9)

- All rates rapid => short lifetimes in PDRs
- Bare carbon chains largest rates
- Odd-numbered C_nH lowest rates

Questions

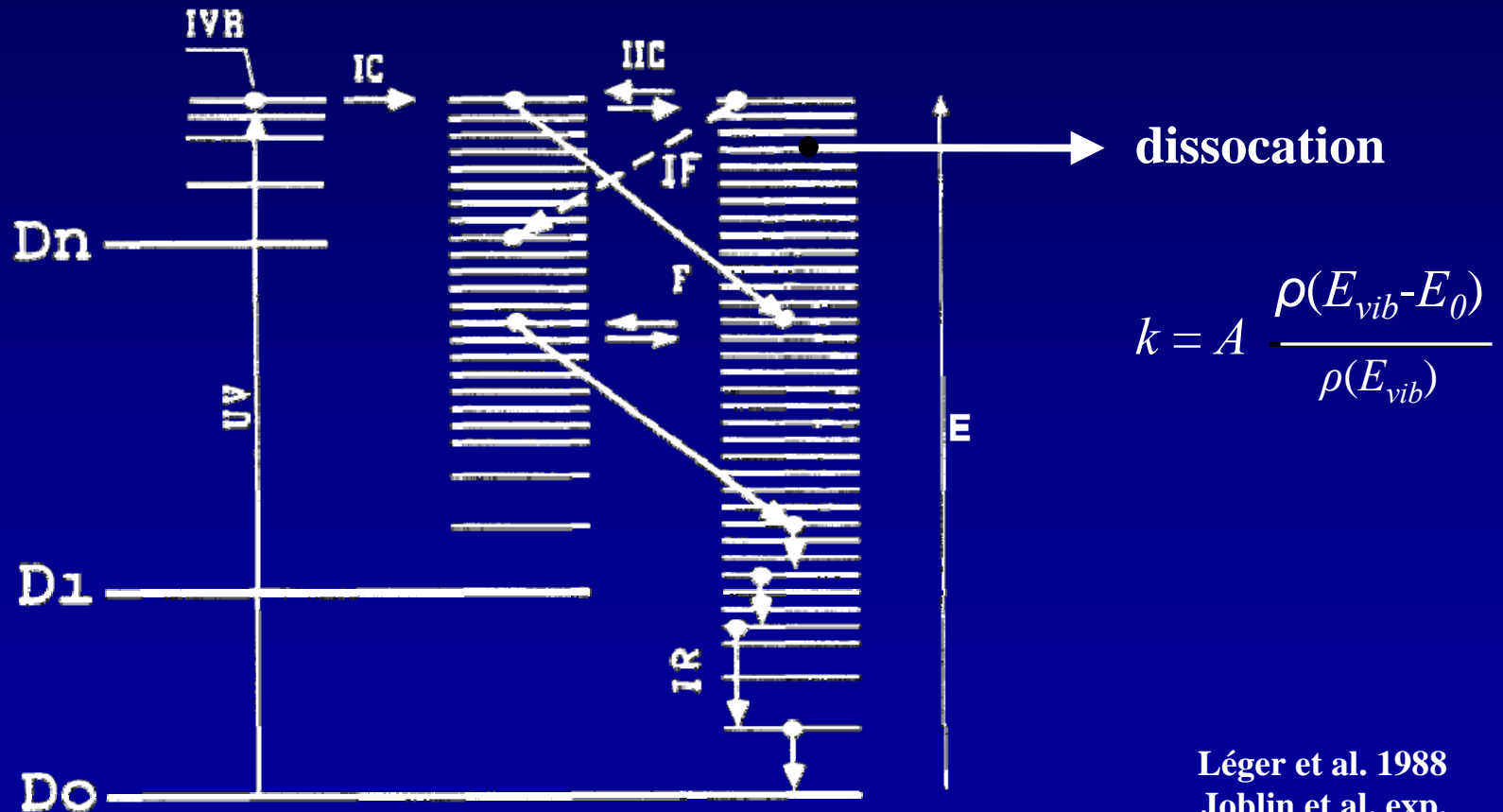
- **How good is assumption that all absorptions above E_{dis} lead to dissociation?**
 - **Some experimental evidence from Choi et al. 2000 for C_4 , where absorption at 5.2-5.4 eV shows $C_3 + C$ production, minor $C_2 + C_2$**
 - **Consistent with phase space theory in which product states are statistical**
 - **Internal conversion to ground state with no barriers to dissociation**
- **Is dissociative ionization important?**
 - ***c*- C_3H_2 has several strong states just above $IP=9.15$ eV**

Large molecules

- Density of vibrational levels of ground state becomes so high that excited states can couple with them non-radiatively: *internal conversion*
 - Alternatives: fluorescence or intersystem crossing followed by phosphorescence
- Some fraction of energy will end up in vibrational mode leading to dissociation; rest will cascade by infrared photons
- Main question: when does molecule become stable against photodissociation? When $N > 25$?
- Large molecules have first IP around 7 eV => (dissociative) photoionization?

Photodestruction PAHs

- UV absorption → hydrogen loss followed by carbon loss

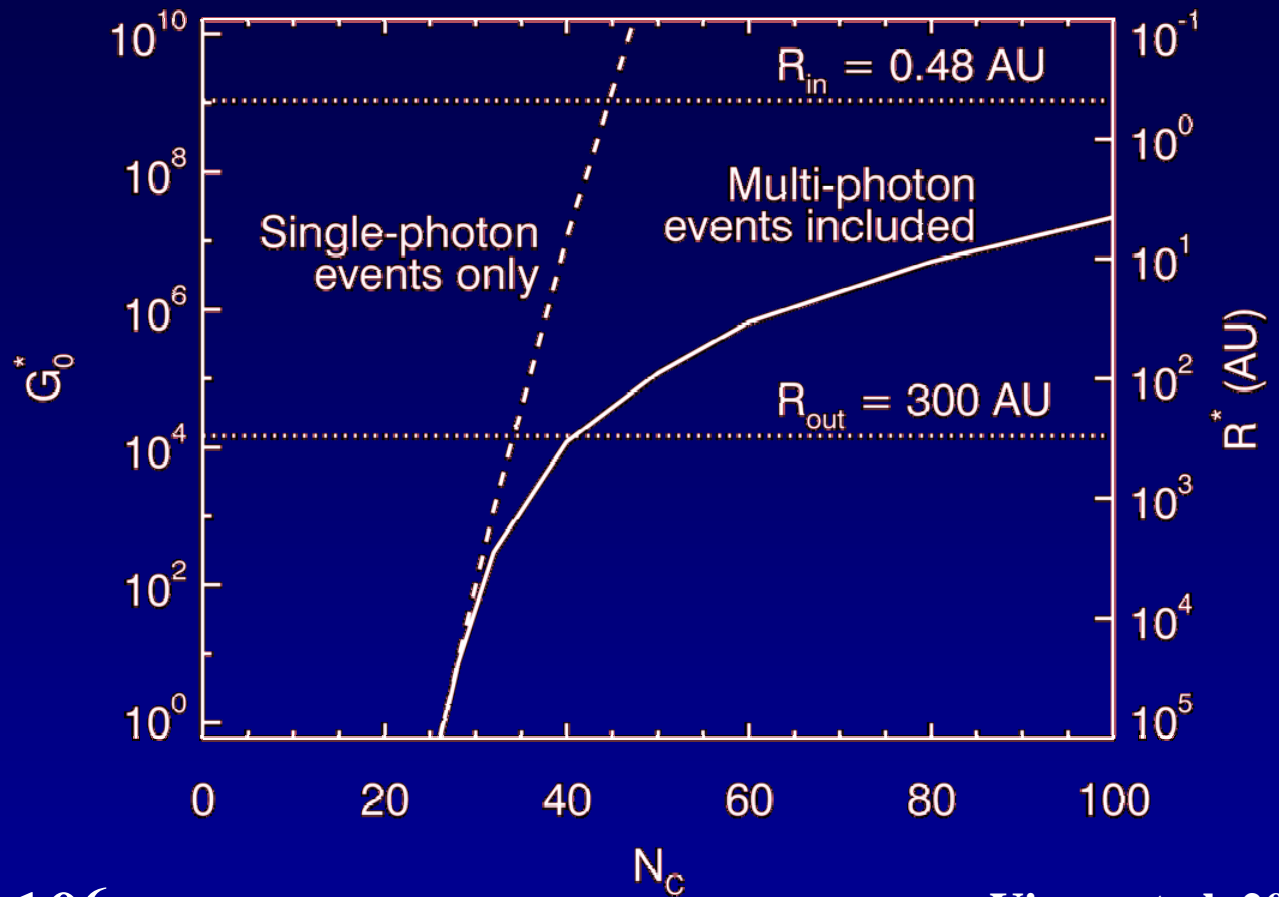


$$k = A \frac{\rho(E_{vib} - E_0)}{\rho(E_{vib})}$$

Léger et al. 1988
Joblin et al. exp.
Visser et al. 2007

PAH destruction in disks

Multi-photon events are important



Destruction in 10^6 yr:

Visser et al. 2007

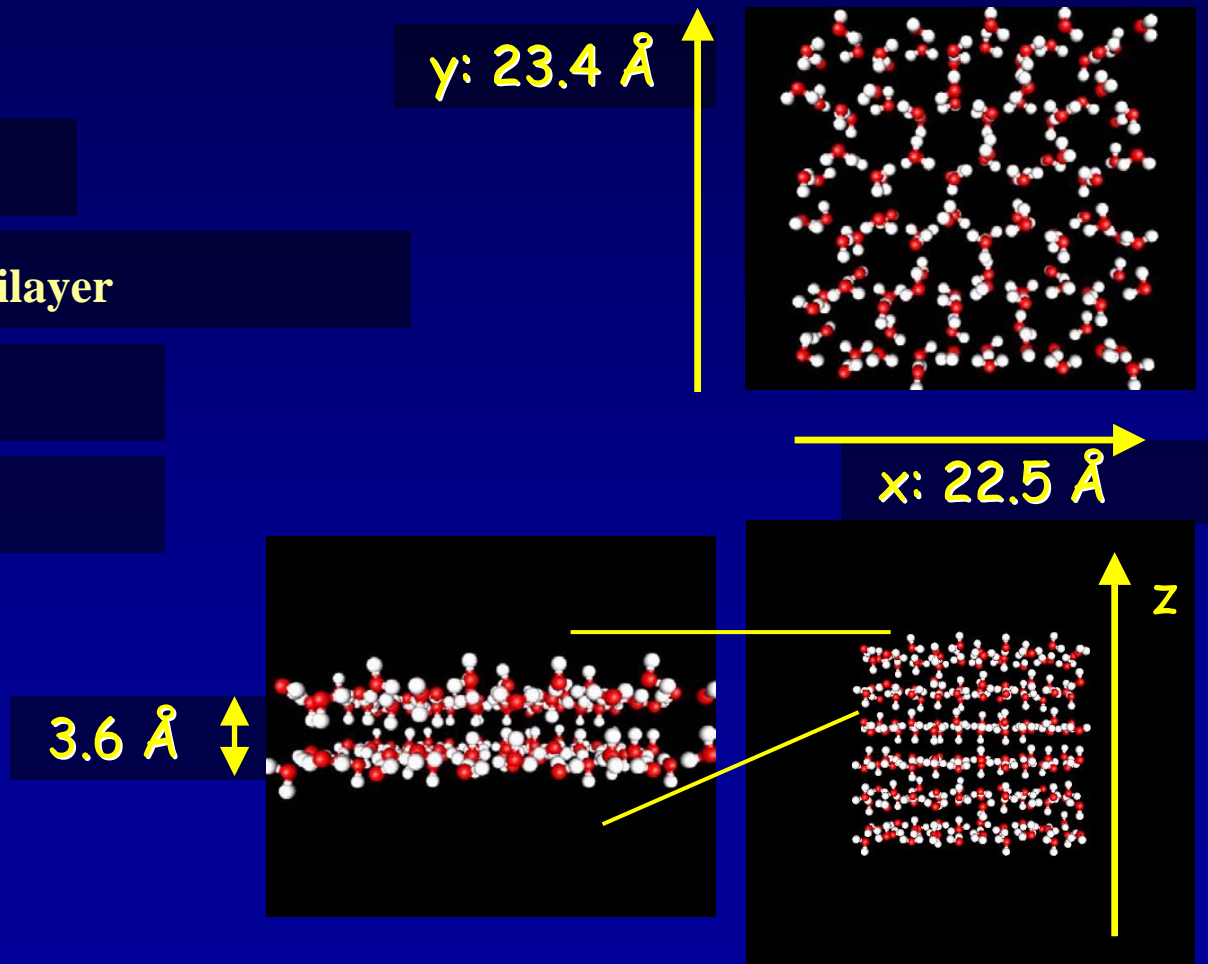
- $N_C < 40$: entire disk
- $N_C > 40$: part of disk → only $N_C = 100$ survives as close as few AU from the star

PDRs in disks vs. clouds

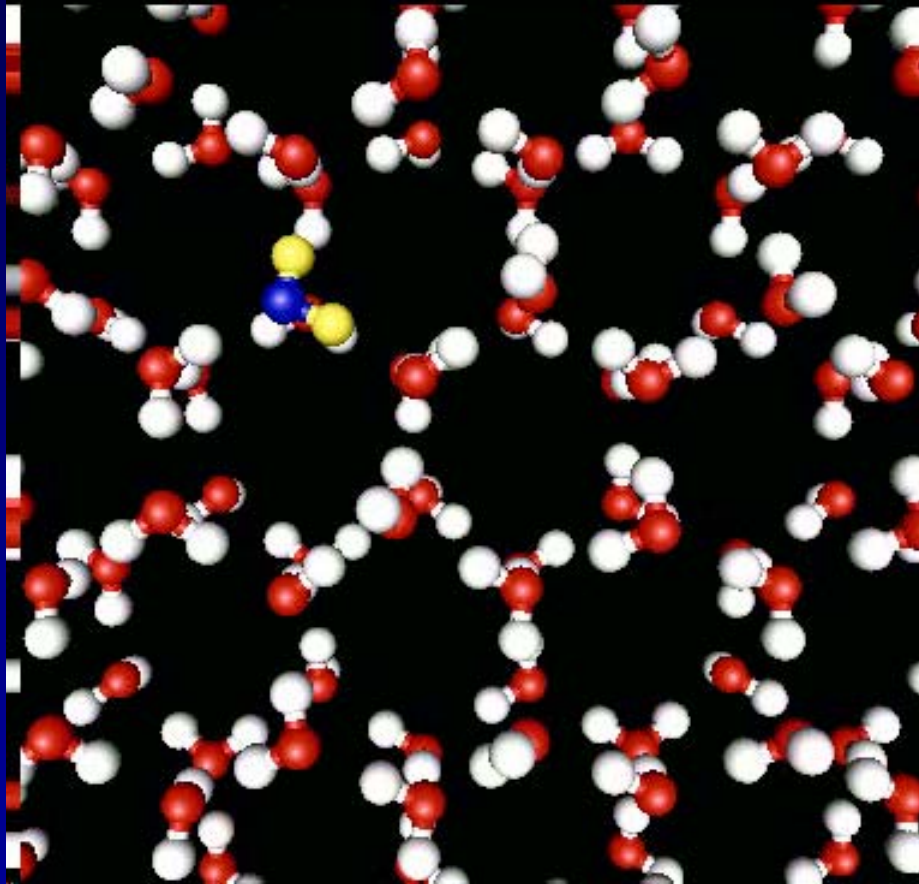
- **Spectral shape radiation field: 30000=>4000 K**
 - **Affects H₂, CO, C p.i., CN, N₂, ...**
 - => *rates as function of T_{eff}*
 - **Resonance lines: Lyman α**
 - => *cross sections at 1216 Å*
- **High intensity radiation fields up to 10⁷xISRF**
 - **Photodissociation of ions important?**
 - => *new calculations of small species*
- **Grains grown to μm size**
 - => *rates for larger grains*
- **Gas/dust mass ratio not equal to 100 (> or <?)**
- **Photodesorption of ices**

Interaction photons with ices: molecular dynamics study of H₂O

- Periodic slab of crystalline ice (Ih)
- 8 bilayers
- 6 moving bilayers
- 60 H₂O molecules per bilayer
- Rigid H₂O molecules
- Classical dynamics



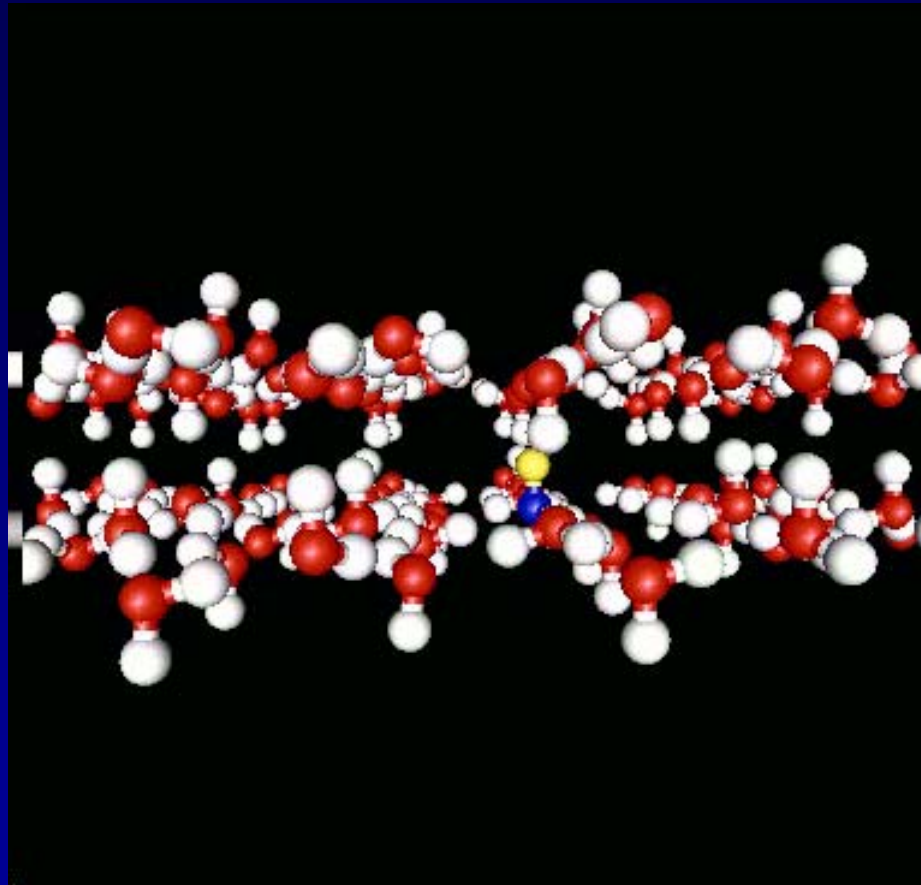
Photodissociation of H₂O ice



Top view

Two top bilayers; molecule in 1st bilayer
Duration: 0.4 ps

Photodissociation of H₂O ice

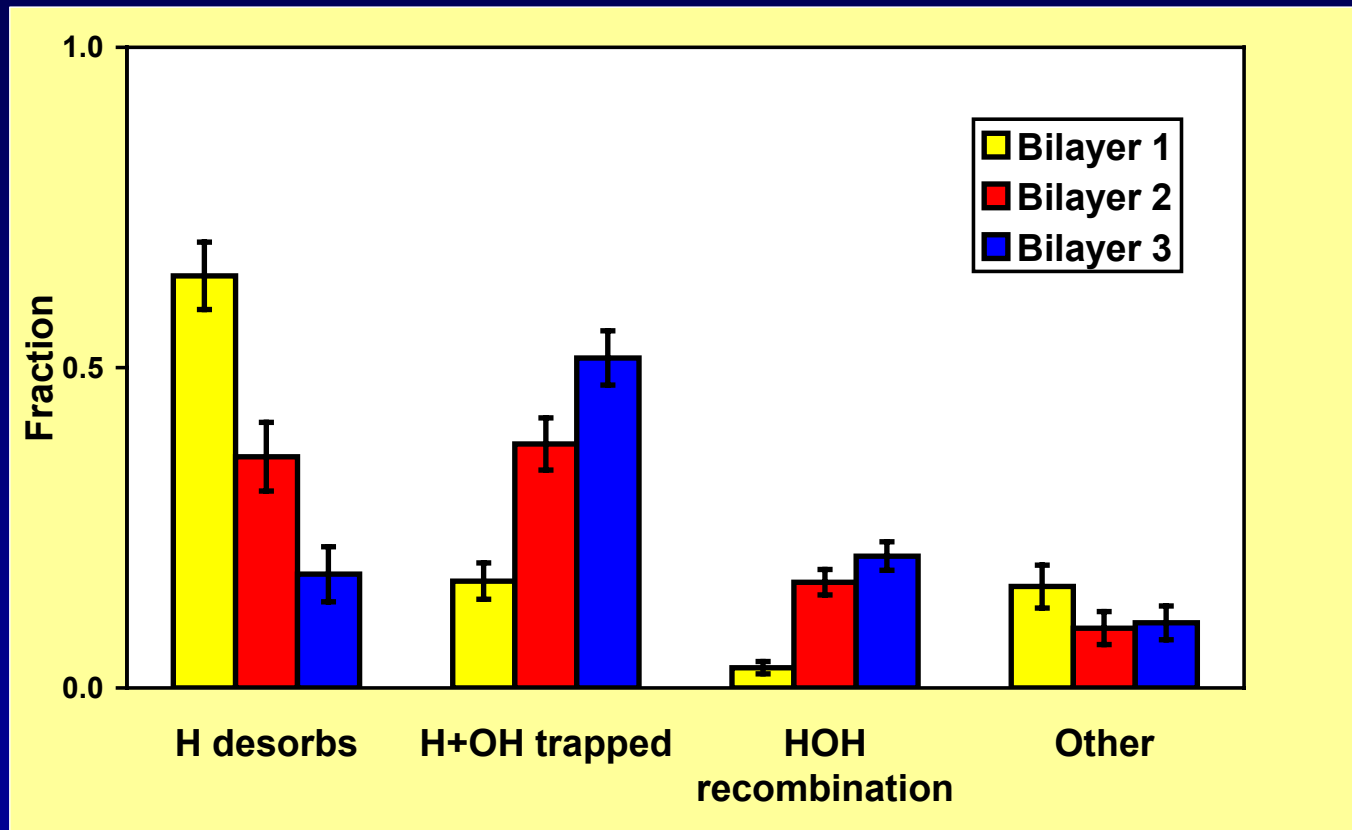


Side view

Two top bilayers; molecule in 2nd bilayer
Duration: 0.6 ps

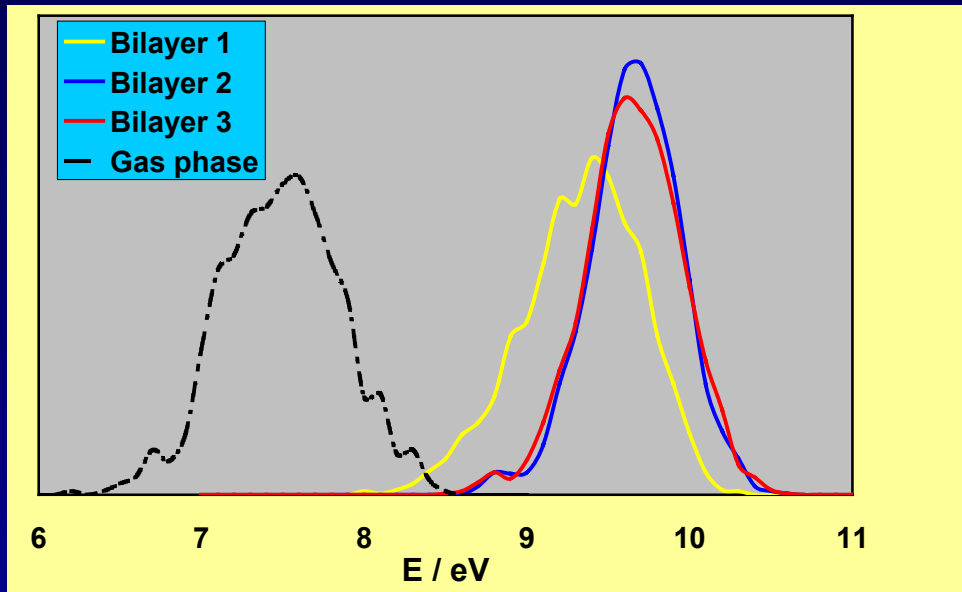
Results

Outcome of photodissociation



- The probability of H desorption decreases by ~50% per bilayer
- 20% recombination in third bilayer

Results absorption spectrum



Peaks

Gas phase: 7.5 eV

1st bilayer: 9.4 eV

2nd and 3rd bilayer: 9.6 eV

Exp.: 8.6 eV

- See compilation of ice absorption spectra various species by Mason et al. (2006)

Conclusions

- **Diatomics: accurate rates, except for heavy diatomics dominated by predissociation**
- **Triatomics: simplest hydrides accurate (including products), but becomes more uncertain if not measured**
- **Polyatomics: smaller O.K. if measured; within factor of few if vertical spectrum calculated. Products highly uncertain**

Future work

- **Finalize comparison with other databases**
- **Update CO isotopic photodissociation**
- **N₂ photodissociation?**
- **Requests for other (calculable) molecules?**
- **Stimulate experimentalists to do large molecules over broad wavelength range**
- **More work on ices**