Photodissociation

Ewine F. van Dishoeck
Leiden Observatory/MPE

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

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: $\text{H}_2^+$, OH, H$_2$O

Predissociation
Ex: CO

Coupled states p.d.
Ex: OH

Spontaneous Radiative dissociation
Ex: H$_2$
Potential curves for $\text{H}_2^+$ 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

\[ k_{pd} = \int_{912}^{\infty} \sigma_{pd}(\lambda)I(\lambda)d\lambda \]

where \( \sigma_{pd} \) 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 \( \eta \) is the dissociation probability
Interstellar radiation field

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 ~50%
Cosmic-ray induced radiation

\[ \text{H}_2 + \text{CR} \rightarrow \text{H}_2^+ + \text{e}^* \]
\[ \text{H}_2 + \text{e}^* \rightarrow \text{H}_2^* + \text{e} \]
\[ \text{H}_2^* \rightarrow \text{H}_2 + \text{hv} \]

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

Stephens & Dalgarno 1970
Gredel et al. 1987
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

See van Dishoeck et al. 2006
A0 star radiation field vs. scaled ISRF

- Results sensitive to adopted UV field, especially <1100 Å
- Affects some molecules, but not all

Joknheid et al. 2006
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

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

- Depends on $\lambda$, grain properties: drops from 3 to 0.6 for $\mu$m 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

vd, vH & Dalgarno 1982
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 H₂O Å – X and higher transitions
  - Detailed predictions of product energy distributions, e.g., OH rotational excitation
  - Similar calculations for CH₂, NH₂, HCO⁺
  - Very difficult for heavier triatomics
  - Ions, especially O-containing ones, lower rates

Kroes et al. 1993; Harrevelt & van Hemert 2000-200x
Time-dependent wavepacket dynamics

From 1D => 3D

CD vs CH

Also: branching ratio to C + H₂ vs CH + H

Kroes, Bearda, vD, vH 1993-5
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 $E_{\text{dis}}$ and below $E_{\text{ion}}$ 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: CH$_4$

Lee & Chiang 1983

High accuracy
Example: $O_2$

High accuracy
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
  - OH $\rightarrow$ O($^3P$), O($^1D$), O($^1S$)
  - CH$^+$ $\rightarrow$ C + 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
Small carbonaceous molecules

- Use increased computing power to determine vertical excitation energies and oscillator strengths of 9 states per symmetry of heavier species
- C₃, C₄, C₂H, l- and c-C₃H, l- and c-C₃H₂, HC₃H, l-C₄H and l-C₅H
- Compute $E_{\text{dis}}$ and IP
- Assume all absorptions above $E_{\text{dis}}$ and below IP lead to dissociation

Caveats

- Comparison with exp and other calculations shows that $E_{\text{ex}}$ accurate to 0.2-0.3 eV and $f$ to better than 30% for lower states
- Higher states ($\geq 5$’th root per symmetry) difficult to calculate because of heavy mixing of states and orbitals
  - $E_{\text{ex}}$ 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Rate ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$-$C_3$</td>
<td>$5.0(-9)$</td>
</tr>
<tr>
<td>$l$-$C_4$</td>
<td>$8.5(-9)$</td>
</tr>
<tr>
<td>$l$-$C_2H$</td>
<td>$1.6(-9)$</td>
</tr>
<tr>
<td>$l$-$C_3H$</td>
<td>$1.8(-9)$</td>
</tr>
<tr>
<td>c-$C_3H$</td>
<td>$1.1(-9)$</td>
</tr>
<tr>
<td>$l$-$C_4H$</td>
<td>$3.7(-9)$</td>
</tr>
<tr>
<td>$l$-$C_5H$</td>
<td>$1.3(-9)$</td>
</tr>
<tr>
<td>HC$_3$H</td>
<td>$2.2(-9)$</td>
</tr>
<tr>
<td>c-$C_3H_2$</td>
<td>$1.4(-9)$</td>
</tr>
<tr>
<td>$l$-$C_3H_2$</td>
<td>$5.1(-9)$</td>
</tr>
</tbody>
</table>

- All rates rapid $\Rightarrow$ short lifetimes in PDRs
- Bare carbon chains largest rates
- Odd-numbered $C_nH$ lowest rates
Questions

- How good is assumption that all absorptions above $E_{\text{dis}}$ 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 $7 \text{ eV} \Rightarrow$ (dissociative) photoionization?
Photodestruction PAHs

- UV absorption $\rightarrow$ hydrogen loss followed by carbon loss

\[ k = A \frac{\rho(E_{\text{vib}} - E_0)}{\rho(E_{\text{vib}})} \]

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

Visser et al. 2007
PDRs in disks vs. clouds

- Spectral shape radiation field: $30000\rightarrow4000$ K
  - Affects H$_2$, CO, C p.i., CN, N$_2$, ...
    - $\Rightarrow$ rates as function of $T_{\text{eff}}$
  - Resonance lines: Lyman $\alpha$
    - $\Rightarrow$ cross sections at 1216 Å

- High intensity radiation fields up to $10^7\times$ISRF
  - Photodissociation of ions important?
    - $\Rightarrow$ new calculations of small species

- Grains grown to $\mu$m size
  - $\Rightarrow$ rates for larger grains

- Gas/dust mass ratio not equal to 100 ($>$ or $<$?)

- Photodesorption of ices
Interaction photons with ices: molecular dynamics study of H$_2$O

- Periodic slab of crystalline ice (Ih)
- 8 bilayers
- 6 moving bilayers
- 60 H$_2$O molecules per bilayer
- Rigid H$_2$O molecules
- Classical dynamics

Andersson et al. 2005
Photodissociation of H₂O ice

Two top bilayers; molecule in 1st bilayer
Duration: 0.4 ps
Photodissociation of $\text{H}_2\text{O}$ ice

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

- 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
- \( \text{N}_2 \) photodissociation?
- Requests for other (calculable) molecules?
- Stimulate experimentalists to do large molecules over broad wavelength range
- More work on ices