The Emission Spectrum due to Molecule Formation through Radiative Association

Magnus Gustafsson

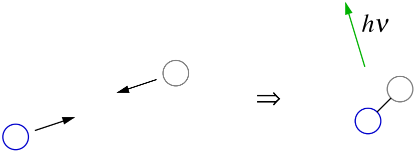
UNIVERSITY OF GOTHENBURG

22^{nd} International Conference on Spectral Line Shapes
The University of Tennessee Space Institute
June 5, 2014

Outline

- What is radiative association?
- How is it calculated?
- Formation of HF: cross sections and emission spectra

Radiative association



- Important for molecule formation in dust-poor regions of the interstellar medium
- Stars and solar systems are born in molecular clouds, like the Orion Nebula
- Laboratory measurements difficult – only done with ionic species
- Why theoretical study of emission spectra?
  - source of radiation in planetary atmospheres
  - potential probe in laboratory

Cross section: quantum mechanical perturbation theory

$$M_{\Lambda EJ,\Lambda' v' J'} = \int_0^\infty F^{\Lambda}_{EJ}(R)\; D_{\Lambda\Lambda'}(R)\; \Phi^{\Lambda'}_{v'J'}(R)\; dR$$

E = asymptotic kinetic energy
$F^{\Lambda}_{EJ}(R)$ = continuum wave function
$D_{\Lambda\Lambda'}(R)$ = transition dipole between electronic states Λ and Λ'
$\Phi^{\Lambda'}_{v'J'}(R)$ = bound state wave function

$$\sigma_{\Lambda\to\Lambda' v' J'}(E) = \frac{2}{3}\frac{h^2}{(4\pi\epsilon_0)c^3}\frac{1}{2\mu E}\; P_\Lambda \sum_J \omega^3_{E\Lambda' v' J'}\; S_{\Lambda J\to\Lambda' J'}\; M^2_{\Lambda EJ,\Lambda' v' J'}$$

$\omega_{E\Lambda' v' J'}$ = angular frequency of emitted photon
$S_{\Lambda J\to\Lambda' J'}$ = Hönl–London factors

$$\sigma_{\Lambda\to\Lambda'}(E) = \sum_{v'J'} \sigma_{\Lambda\to\Lambda' v' J'}(E)$$

Cross section: classical theory (no electronic transition)

Based on the Larmor power:

$$\hat{I}(b, E, \omega) = P_\Lambda \frac{2\omega^4}{3c^3\pi(4\pi\epsilon_0)} \left| \int_{-\infty}^{\infty} dt \; e^{i\omega t} \; \mathbf{D}_{\Lambda\Lambda}(b, E, t) \right|^2$$

with the dipole moment $\mathbf{D}_{\Lambda\Lambda}(b, E, t)$ evaluated along a trajectory with initial energy E and impact parameter b.

Spectral density:

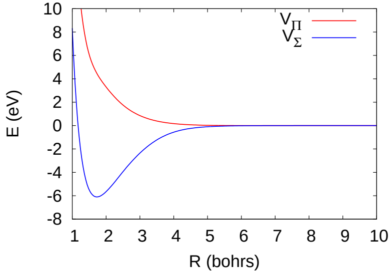
$$\frac{d\sigma_{\Lambda\to\Lambda}(E)}{d\omega} = \int_0^\infty 2\pi b \frac{\hat{I}(b, E, \omega)}{\hbar\omega} \; db$$

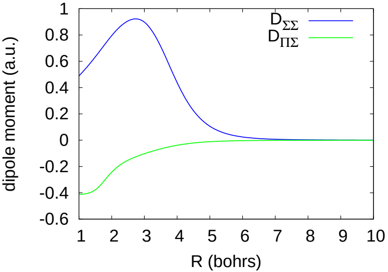
Radiative association cross section:

$$\sigma_{\Lambda\to\Lambda}(E) = \int_{E/\hbar}^{\omega_2} \frac{d\sigma_{\Lambda\to\Lambda}(E)}{d\omega} \; d\omega$$

with the limits, $E/\hbar$ and ω_2, defined by the range of bound states.

HF potentials and dipole moments



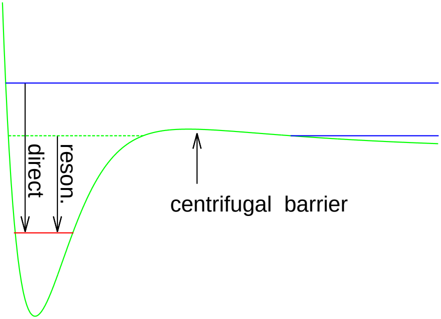


Radiative association reactions:

$$\mathrm{H}(^2S) + \mathrm{F}(^2P) \rightarrow \mathrm{HF}(A^1\Pi) \rightarrow \mathrm{HF}(X^1\Sigma^+) + \hbar\omega \qquad \text{called } \Pi \rightarrow \Sigma$$

$$\mathrm{H}(^2S) + \mathrm{F}(^2P) \rightarrow \mathrm{HF}(X^1\Sigma^+) \rightarrow \mathrm{HF}(X^1\Sigma^+) + \hbar\omega \qquad \text{called } \Sigma \rightarrow \Sigma$$

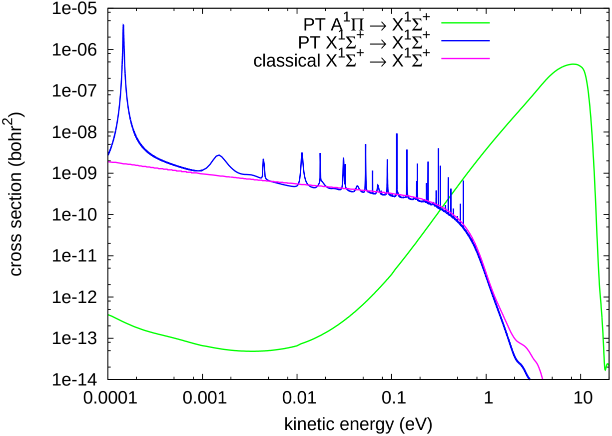
Radiative association mechanisms



HF $\Pi \rightarrow \Sigma$: only direct

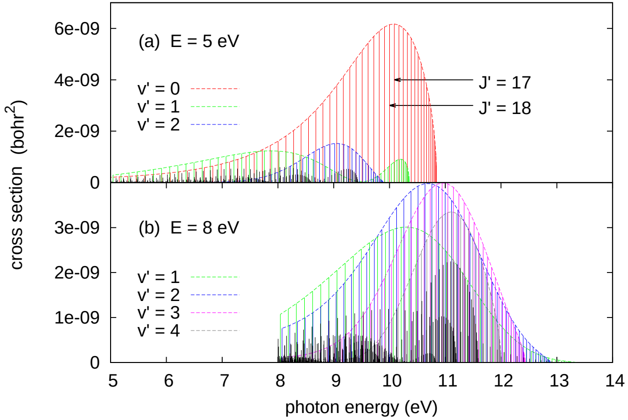
HF $\Sigma \rightarrow \Sigma$: both direct and resonance mediated

HF radiative association cross sections



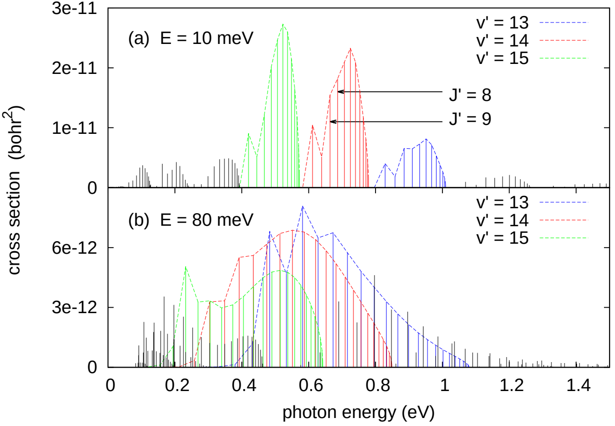
PT = quantum mechanical perturbation theory

HF $\Pi \rightarrow \Sigma$ radiative association emission spectra

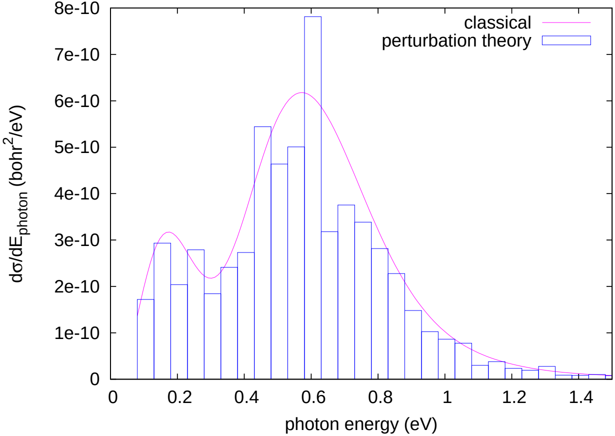


final state resolved cross section $\sigma_{\Lambda \rightarrow \Lambda' v' J'}(E)$

HF $\Sigma \rightarrow \Sigma$ radiative association emission spectra

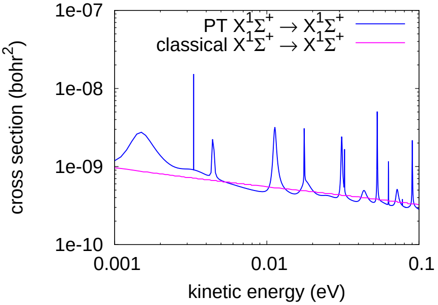


HF $\Sigma \rightarrow \Sigma$ radiative association spectral density



$E = 80$ meV

HF $\Sigma \to \Sigma$ resonance mediated radiative association



The narrow resonance at $E =$ 3.304 meV has v=18, J=13, and peak value $\sigma = 9.0$ bohr^2

Contributions:

v'	J'	σ (bohr^2)	E_{photon} (eV)
13	12	1.1	0.79
13	14	1.2	0.72
14	12	1.2	0.58
14	14	2.3	0.51

Conclusion

Radiative association of HF:

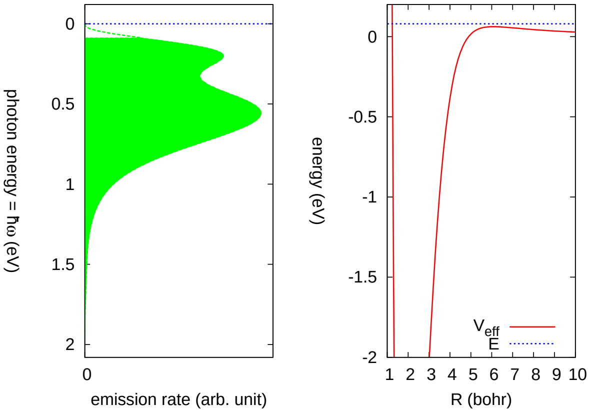
- 1–6 μm emission (IR) at low energies
- 100–150 nm emission (UV) at high energies
- resonance mediated emission could allow detection of emitted photons in laboratory experiments

Acknowledgments

- Gunnar Nyman
- The Swedish Science Council

Thank you!

Intermediate result with classical approach for H+F collisions



E=80 meV
b=6 bohrs

emission rate $= \hat{I}(b, E, \omega)/\omega$

effective potential $= V_\Sigma(R) + \frac{Eb^2}{R^2}$

The shaded area under the emission curve corresponds to HF formation through radiative association.

Breit–Wigner theory

The contribution to the cross section from one resonance:

$$\sigma(E, v', J') \quad = \quad \frac{\pi\hbar^2}{2\mu E}\; p\;(2J'+1)\frac{\Gamma^{\rm rad}_{v'J'}\Gamma^{\rm tun}_{v'J'}}{(E-E_{v'J'})^2+(\Gamma^{\rm tun}_{v'J'}+\Gamma^{\rm rad}_{v'J'})^2/4}$$

- $E_{v'J'}$ is the energy of the quasi-bound level
- $\Gamma^{\rm tun}_{v'J'}$ is the tunneling width
- $\Gamma^{\rm rad}_{v'J'}$ is the radiative width for spontaneous emission

$E_{v'J'}$, $\Gamma^{\rm tun}_{v'J'}$, and $\Gamma^{\rm rad}_{v'J'}$ can be calculated fast without solving the full scattering problem (e.g. with LeRoy's LEVEL program).