The emission spectrum due to molecule formation through radiative association

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Abstract. Quantum mechanical and classical methods for theoretical analysis of the emission spectrum due to radiative association are presented. Quantum mechanical perturbation theory is employed to obtain the spectra when the diatomic molecule HF forms by transitions within the electronic ground state and when it forms by transitions between two electronic states. We contrast these spectra with each other. The former peaks in the infrared, while the latter peaks in the ultraviolet. The classical spectrum, which concerns transitions within the electronic ground state, is also calculated and found to favorably compare with that from quantum mechanical perturbation theory. The emission stemming from resonance mediated radiative association is also discussed.

1. Introduction
Radiative association is a mechanism which contributes to the production of molecules in interstellar clouds. It is especially important in low-density and dust-poor regions where reactions due to ternary collisions are extremely rare [1]. On Earth the rates for radiative association reactions are typically orders of magnitude lower than those of other chemical processes, such as exchange reactions, and direct laboratory measurements have so far only been possible to carry out for certain ionic systems [2]. Thus astronomers who wish to model the chemical evolution in interstellar space often have to rely on theoretical calculations of radiative association rates. Not only molecular formation due to radiative association but also the corresponding emission spectrum has attracted attention. For example, radiative association of N and O atoms is a significant source of emission in the terrestrial nightglow and in the atmosphere of Venus [3]. In this work we analyze the emission spectrum due to formation of HF at different relative kinetic energies of the colliding atoms H and F. Some of the theory and the results are presented in more detail in Ref. [4].

2. Theory
In general it is desirable to Boltzmann average the cross sections for radiative association in order to obtain thermal rate constants. The focus here is on the spectra, however, which are conveniently analyzed through the energy dependent cross sections. In sections 2.1, 2.2, and 2.3 we will briefly outline three different approximations to obtain the cross sections. In section 2.4 some theoretical aspects of radiative association of HF are presented.
2.1. Quantum mechanical perturbation theory

Perturbation theory for dipole transitions, or Fermi’s golden rule, hinges on the evaluation of transition dipole matrix elements

\[ M_{\Lambda EJ,\Lambda'v'J'} = \int_{0}^{\infty} F_{EJ}^\Lambda(R) \ D_{\Lambda \Lambda'}(R) \ \Phi_{\Lambda'v'J'}(R) \ dR \]

where \( E \) is the asymptotic relative kinetic energy for the colliding particles, \( F_{EJ}^\Lambda(R) \) is the continuum wave function, and \( \Phi_{\Lambda'v'J'}(R) \) is the bound state wave function. \( D_{\Lambda \Lambda'}(R) \) is the electric transition dipole between electronic states \( \Lambda \) and \( \Lambda' \) if \( \Lambda \neq \Lambda' \) and the permanent electric dipole moment if \( \Lambda = \Lambda' \). The cross section for (spontaneous emission) radiative association of a molecule in rovibrational state \( \nu', J' \) is obtained through [5]

\[ \sigma_{\Lambda \rightarrow \Lambda'v'J'}(E) = \frac{2}{3} \frac{\hbar^2}{(4\pi\epsilon_0)c^3} \ \frac{1}{2\mu E} \ P_{\Lambda} \ \omega_{E\Lambda'v'J'}^3 \ \sum_{J} S_{\Lambda J \rightarrow \Lambda' J'} \ M_{\Lambda EJ,\Lambda'v'J'}^2 \]

where \( \omega_{E\Lambda'v'J'} \) is the angular frequency of emitted photon and \( S_{\Lambda J \rightarrow \Lambda' J'} \) are Hön–London factors [6]. \( P_{\Lambda} \) is the statistical weight for approach in the electronic state \( \Lambda \), i.e. the degeneracy of state \( \Lambda \) divided by the total degeneracy. Specific values for \( P_{\Lambda} \) are given in section 2.4. The total radiative association cross section for formation of a molecule by transition from electronic state \( \Lambda \) to \( \Lambda' \) is obtained by summation over all final vibrational and rotational quantum numbers, i.e.

\[ \sigma_{\Lambda \rightarrow \Lambda'}(E) = \sum_{v'J'} \sigma_{\Lambda \rightarrow \Lambda'v'J'}(E) \]

2.2. Classical theory (no electronic transition)

In the purely classical treatment of radiative association within one electronic state the radiation is given by the Larmor power [7]

\[ \dot{I}(b, E, \omega) = P_{\Lambda} \ \frac{2\omega^4}{3e^3\pi(4\pi\epsilon_0)} \ \left| \int_{-\infty}^{\infty} dt \ e^{i\omega t} \ \textbf{D}_{\Lambda\Lambda}(b, E, t) \right|^2 \]

with the time dependent dipole moment \( \textbf{D}_{\Lambda\Lambda}(b, E, t) \) evaluated along a classical trajectory with initial energy \( E \) and impact parameter \( b \). The spectral density can be obtained as

\[ \frac{d\sigma_{\Lambda \rightarrow \Lambda'}(E)}{d\omega} = \int_{0}^{\infty} 2\pi b \ \frac{\dot{I}(b, E, \omega)}{\hbar \omega} \ db \]
Figure 3. Schematic illustration of direct and resonance mediated radiative association. In this case the process takes place within one electronic state, as is the case for reaction (10). The resonance mediated process thus gives rise to shape resonances in the cross section. In general several electronic states may be involved, which can give rise to both shape and Feshbach resonances.

and finally the radiative association cross section is computed by integration over photon energies [8]

$$\sigma_{\Lambda \rightarrow \Lambda}(E) = \int_{E/h}^{\omega_2} \frac{d\sigma_{\Lambda \rightarrow \Lambda}(E)}{d\omega} \, d\omega$$

with the limits, $E/h$ and $\omega_2$, defined by the range of bound states.

2.3. Breit–Wigner theory

Radiative association cross sections are often rich in sharp resonance features. This makes it numerically hard to thermally average them to obtain rate constants. Breit–Wigner theory [9, 10] provides a convenient way to get around this problem. The cross section for radiative association, mediated through quasibound states with rotational and vibrational quantum numbers $J$ and $v$, respectively, is

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

where the state resolved cross is defined by

$$\sigma_{\Lambda vJ \rightarrow \Lambda' v'J'}(E) = \frac{\pi \hbar^2}{2\mu E} P_{\Lambda} (2J + 1) \frac{\Gamma_{\Lambda vJ \rightarrow \Lambda' v'J'}^{\text{rad}} \Gamma_{\Lambda vJ \rightarrow \Lambda' v'J'}^{\text{tun}}}{(E - E_{\Lambda vJ})^2 + (\Gamma_{\Lambda vJ}^{\text{tun}} + \sum_{v''J''} \Gamma_{\Lambda vJ \rightarrow \Lambda' v''J''}^{\text{rad}})^2/4}$$

In Eq. (8) $E_{\Lambda vJ}$ is the energy of the quasi-bound level, $\Gamma_{\Lambda vJ}^{\text{tun}}$ is its tunneling width, and $\Gamma_{\Lambda vJ \rightarrow \Lambda' v'J'}^{\text{rad}}$ is its radiative width for allowed $\Lambda vJ \rightarrow \Lambda' v'J'$ spontaneous emission processes. The $v''J''$ summation in the denominator of Eq. (8) could be extended to a summation over more than one final electronic state (A') but here we will only consider radiative decay to one electronic state. The resonance parameters $E_{\Lambda vJ}$, $\Gamma_{\Lambda vJ}^{\text{tun}}$, and $\Gamma_{\Lambda vJ \rightarrow \Lambda' v'J'}^{\text{rad}}$ can be calculated fast without solving the full scattering problem, e.g. with LEVEL [11].
2.4. Radiative association of HF

In this study we consider the radiative association reactions

\[
\begin{align*}
H( ^2S) + F( ^2P) &\rightarrow HF(A^1\Pi) \rightarrow HF(X^1\Sigma^+) + \hbar \omega \\
H( ^2S) + F( ^2P) &\rightarrow HF(X^1\Sigma^+) \rightarrow HF(X^1\Sigma^+) + \hbar \omega
\end{align*}
\]

for formation of HF in its ground electronic state. The factor \( P_{\Lambda} \) which appears in the expressions for the cross sections above is \( 2/12 \) and \( 1/12 \) for reactions (9) and (10), respectively. In the discussion below reactions (9) and (10) will sometimes be referred to as \( A^1\Pi \rightarrow X^1\Sigma^+ \) and \( X^1\Sigma^+ \rightarrow X^1\Sigma^+ \), respectively. The potential energies and electric dipole moments used in the calculations are shown in Figs. 1 and 2. The \( X^1\Sigma^+ \) state potential energy and dipole moment functions are based on the data of Ref. [12], and the \( A^1\Pi \) potential energy and \( A^1\Pi - X^1\Sigma^+ \) transition dipole moment are based on the data of Ref. [13].

Radiative association can occur through two main classes of mechanisms commonly called direct and resonance mediated. The difference between them is illustrated in Fig. 3 and by inspecting the potential curves in Fig. 1 we conclude that reaction (9) only can occur through direct radiative association. This is a consequence of the fact that the \( A^1\Pi \) potential is purely repulsive, except for a tiny van der Waals well, and therefore it does not support any quasibound states. Reaction (10) on the other hand occurs through both mechanisms and will thus have resonance structure.

3. Results

Fig. 4 shows the HF radiative association cross section versus kinetic energy from 0.1 meV to 20 eV. The cross section for reaction (10) dominates up to an energy of about 0.3 eV and at higher energies reaction (9) dominates. In our analysis of the spectra below, we focus on each reaction in the energy range where it dominates. HF radiative association emission spectra versus photon energy, \( \hbar \omega_{EM,v',J'} \), computed quantum mechanically with Eq. (2), are shown in Figs. 5 and 6 for \( A^1\Pi \rightarrow X^1\Sigma^+ \) and \( X^1\Sigma^+ \rightarrow X^1\Sigma^+ \) transitions, respectively. The envelopes corresponding to vibrational quantum states, \( v' \), with dominating cross sections are indicated. The collision energies are chosen to be off-resonance in the \( X^1\Sigma^+ \rightarrow X^1\Sigma^+ \) case. There is a striking difference in photon energies emitted from the two reactions \( A^1\Pi \rightarrow X^1\Sigma^+ \), which emits mostly ultraviolet

\[
\begin{align*}
J' = 17 \\
J' = 18 \\
v' = 0 \\
v' = 1 \\
v' = 2 \\
v' = 3 \\
v' = 4
\end{align*}
\]

Figure 5. Emission spectra for \( A^1\Pi \rightarrow X^1\Sigma^+ \) radiative association of HF at collision energies of 5 eV and 8 eV. Reprinted with permission from [4]. Copyright (2014), American Institute of Physics.

Figure 6. Emission spectra for \( X^1\Sigma^+ \rightarrow X^1\Sigma^+ \) radiative association at collision energies of 10 meV and 80 meV. Reprinted with permission from [4]. Copyright (2014), American Institute of Physics.
radiation in the range 8–12 eV, and $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ which emits mostly infrared radiation in the range from 0.2 to 1.0 eV.

It is also interesting to see how well the classical spectral density given by Eq. 5 compares with its quantum mechanical counterpart. In Fig. 7 the comparison is shown and we see that for this system the quantum mechanical result shows more structure than that from a classical calculation. The general shape, however, is rather similar and, as was noted above in the discussion of Fig. 4, an integration over photon energy gives a classical cross section that agrees with the baseline of the quantum mechanical cross section. The former is only about 12% above the latter.

It cannot be denied that the values of the cross sections presented above are rather small, making it difficult to use measurement of photon emission as a probe of radiative association. At the peaks of the resonances, however, the cross sections can be large. As an example of this we analyze the narrow $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ resonance peak at $E = 3.304$ meV in Fig. 4. The corresponding quasibound state has vibrational and rotational quantum numbers $v=18, J=13$, respectively. Using the Breit–Wigner formula, Eq. (7), to compute the peak value gives a cross section of 9.0 bohr$^2$. The peak is thus by no means resolved in Fig. 4. The contributions to this (9 bohr$^2$) cross section from formation of HF in different rovibrational states can be obtained through Eq. (8). The main contributions are presented in table 1 and we see that those four transitions account for about 2/3 of the cross section.

| $v'$ | $J'$ | $\sigma$ (bohr$^2$) | $E_{\text{photon}}$ (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                    |

4. Conclusions

The emission spectrum due to radiative association of HF is highly dependent on the relative kinetic energy of the colliding H and F atoms. At collision energies below about 0.3 eV, where the molecule formation is due to $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ transitions, the spectrum is most intense in the infrared with wavelengths of about 1–6 μm. At higher energies the molecule formation...
occurs primarily through $A^1\Pi \rightarrow X^1\Sigma^+$ transitions and the emission is dominated by ultraviolet radiation with wavelengths of roughly 100–150 nm. The resonance mediated emission can be rather strong compared to the off-resonance case. For the resonance case that we studied in detail there are four transitions, which all have cross sections that are larger than 1 bohr$^2$, that account for the majority of the peak cross section. Detecting the emitted photons for this kind of process is still expected to be difficult as the total photon count for a narrow resonance like the one we analyzed may be small. The small width of the resonance in turn stems from the fact that the corresponding quasibound state has a long lifetime.

Acknowledgments
This work was supported by the Swedish Science Council.

References
[1] Babb J F and Kirby K P 1998 The Molecular Astrophysics of Stars and Galaxies ed Hartquist T W and Williams D A (Oxford: Clarendon Press) p 11
[2] Gerlich D and Horning S 1992 Chem. Rev. 92 1509
[3] Dalgarno A, Babb J and Sun Y 1992 Planet. Space Sci. 40 243
[4] Gustafsson M, Monge-Palacios M and Nyman G 2014 J. Chem. Phys. 140 184301
[5] Babb J F and Dalgarno A 1995 Phys. Rev. A 51(4) 3021
[6] Hansson A and Watson J K 2005 J. Molec. Spectrosc. 233 169
[7] Levine H B and Birnbaum G 1967 Phys. Rev. 154 86
[8] Gustafsson M 2013 J. Chem. Phys. 138 074308
[9] Breit G and Wigner E 1936 Phys. Rev. 49 519
[10] Bain R A and Bardsley J N 1972 J. Phys. B 5 277
[11] Le Roy R J 2007 University of Waterloo Chemical Physics Research Report CP-663
[12] Talbi D and Bacchus-Montabonel M C 2007 Chem. Phys. Lett. 443 40
[13] Brown A and Balint-Kurti G G 2000 J. Chem. Phys. 113 1870