

FORMATION OF SMALL MOLECULES IN INTERSTELLAR SPACEGunnar Nyman

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It is essential to know the roles of both gas-phase and gas-grain processes for understanding the chemical evolution of the interstellar medium (ISM). Here we discuss the gas phase formation of small molecules through radiative association.

In radiative association two species collide and during the collision a photon is emitted, which carries away enough energy that the fragments become bound to each other. The emission of the photon is an improbable event giving small cross sections for molecule formation through radiative association. However, since the ISM is so dilute, energy loss by the alternative process three-body collisions is even less likely. Therefore, radiative association can still be an important process for forming new molecules, particularly in dust poor regions.

Successful experimental measurements of radiative association rate constants for small molecules are few [1] due to the small cross sections, which typically are several orders of magnitude smaller than for ordinary chemical reactions. The lack of experimental measurements of radiative association cross sections and rate constants enhances the interest to perform theoretical calculations to estimate them. We have performed calculations for the formation of several diatomic molecules by radiation association, viz. CN [2-4], CO [4-7], SiN [8], SiP [9], HF [4,10], OH [11], CF⁺[12], HCl [13], CO⁺[14-15] and CH [16], in some cases including isotopologues.

We use three different methods for calculating the radiative association formation of diatomic molecules [17]. One of the methods is a quantum mechanically based perturbation theory approach where the radiative process is treated as a perturbation to the collision process, which is usually a good approximation as the spontaneous emission of a photon within the short duration of collision between two atoms is an unlikely process. This approach is the most computer intensive of the three methods, partly because it requires all bound states for all total angular momenta that give effective potentials that support bound states. Transitions from a dense energy grid of scattering states to every bound state must thereafter be calculated, which requires the transition dipole moment for transitions between electronic states and permanent dipole moments for transitions within the same electronic state.

Another method that we use we refer to as the semiclassical method. It is based on classical trajectories to follow the motion of the atoms combined with Einstein A-coefficients to find the probability for transition from the initial electronic state to another, which can be worked out using the transition dipole moment for various internuclear separation, which thus must be known. The remaining method we refer to as the classical method and it is based on running classical trajectories and thereby tracking the change in dipole moment as a function of time. From the oscillation of the dipole moment in time the radiated energy is estimated from classical electromagnetism using the Larmor formula [18]. This requires that the permanent dipole moment is known as a function of internuclear separation.

The perturbation theory approach is applicable both to processes where photon emission leads to transitions within the same electronic state and when it leads to transitions between electronic states. The semiclassical approach is only valid for transitions between electronic states, while the classical method only is valid for transitions within the same electronic state. Using all three methods gives us the possibility to apply two different methods to study each

of these two types of transitions in the formation of diatomic molecules through radiative association, which helps in judging the reliability of the results.

Resonances are common in radiative association and this means that the calculated transition probabilities can change quickly with collision energy. The resonances can contribute substantially to the cross sections. Resonances are only included in the perturbation theory approach and not in the other two methods that we use. The resonance contribution can however be estimated by Breit-Wigner theory [19], for instance by using the LEVEL program developed by Le Roy [20]. We can therefore separately calculate the resonance contribution and thus add it to the semiclassical or classical results and again, this helps in judging the validity of our results.

We have also performed quantum dynamical calculations of cross sections and rate constants for the radiative association formation of a few triatomic molecules, viz. HCO [21], $(\text{Na-H}_2)^+$ [22], $(\text{Na-D}_2)^+$ [22], $(\text{Al-H}_2)^+$ [23], and $(\text{Al-D}_2)^+$ [23]. These calculations have all been performed in collaboration with Thierry Stoecklin, who has developed a quantum dynamics code for performing such calculations. Below we exemplify some of our calculations for the radiative formation of diatomic and triatomic molecules.

CO and HCO may be important species in the formation of complex organic molecules in interstellar space. Tielens and Hagen proposed in the early 80'ies that a possible route for methanol formation could be to successively add H to CO [24]:



The formation of CO by radiative association was calculated for forming the two isotopologues ^{12}CO and ^{13}CO [6]. Surprisingly large isotope effects were obtained. At some temperatures of interstellar interest the thermal rate constants differ by two orders of magnitude, which we found to be due to quite different resonance structures for the two isotopologues. We note that the resonance structure depends sensitively on the potential energy curve as it decides the energetic position of the quasibound rovibrational levels for the two isotopologues, which differs due to the different masses. Tunnelling into the quasibound states gives rise to most of the resonance structure and is sensitive to which isotopologues is studied.

The potential energy surface for the H+CO reaction has a barrier of 3.3 kcal/mol. For this reason, the radiative association thermal rate constants that we calculate are so small that in the cold interstellar medium radiative association cannot be the first step in the sequence shown above leading to the formation of methanol.

Radiative association thermal rate constants for forming $(\text{Na-H}_2)^+$ from H_2 and Na^+ have previously been estimated by Smith et al. to be 4×10^{-19} cm³/s at 20 K [25] and by Petrie & Dunbar to be 9×10^{-23} at 30 K [26]. The former value is large enough that radiative formation to form $(\text{Na-H}_2)^+$ should be included in chemistry models of dense molecular clouds, while the latter is not. We thus found it interesting to make an accurate quantum dynamics calculation of the rate constant for $(\text{Na-H}_2)^+$ formation by radiative association.

We find the radiative association rate constant for forming $(\text{Na-H}_2)^+$ to be about three orders of magnitude larger than the value of Petrie & Dunbar, but about a factor of ten smaller than the value of Smith et al. Still, our value is large enough that radiative association formation to form $(\text{Na-H}_2)^+$ should be included in chemistry models of dense molecular clouds. We also find a large isotope effect in that the rate constant for forming $(\text{Na-D}_2)^+$ is about two orders of

magnitude larger than the one for forming $(\text{Na-H}_2)^+$. This is largely a result of the larger density of bound states for $(\text{Na-D}_2)^+$ than for $(\text{Na-H}_2)^+$ and that larger angular momenta contribute to the formation of $(\text{Na-D}_2)^+$.

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