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Radiative and collisional processes in space chemistry

M. C. Bacchus-Montabonel

Abstract The theoretical treatment of radiative association and charge transfer processes is developed using ab initio molecular calculations. Semi-classical and quantal dynamical approaches are presented for the determination of cross sections and rate constants which are important data for space chemistry models. Results are detailed for two specific reactions illustrating these important processes: the formation of H_2O by radiative association in the atmosphere of evolved stars in the high temperature region and the $C^+(^2P) + S(^3P) \rightarrow C(^3P) + S^+(^4S)$ charge transfer process which is a fundamental reaction of the interstellar medium which drives the ionization balance of carbon and sulphur.

Keywords Quantum chemical calculations · Collision dynamics · Vibration analysis · Radiative association · Charge transfer

1 Introduction

Radiative and collisional processes play an important role in space chemistry. Such reactions may be involved in the description of a number of environments, as astrophysical plasmas, atmosphere of stars, interstellar medium and so on, and the knowledge of their rate constants is determinant in the modelization of these mediums. In that sense, two main mechanisms are presented in this paper. First of all, the radiative association reaction, fundamental in the early universe chemistry for the formation of simple diatomic molecules as H_2, HD or LiH assumed to be crucial in the description of the spherical collapse of primordial gas clouds (Dubrovich 1977). Such process has also been proposed for the formation of H_2O from atomic oxygen and H_2 in the high atmosphere of stars in the 1,500–3,000 K temperature region and an analysis of recent results is developed (Talbi and

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Bacchus-Montabonel 2010). Secondly, we consider the charge transfer between multiply charged ions and neutral targets. This is a fundamental process for the description of the interstellar medium which drives the ionization balance of charged species. Effectively, a quantitative analysis of the emission-line spectra of ionized astronomical objects requires reliable data on the microscopic ionization and recombination processes involved. The recombination of multiply charged ions by charge transfer with atomic hydrogen or helium is particularly important in astrophysical plasmas (Honvault et al. 1995; Vaeck et al. 2001). Recently, we have investigated more specifically the $C^+(^2P) + S(^3P) \rightarrow C(^3P) + S^+(^4S)$ charge transfer process which is one of the main reaction for the carbon and sulphur chemistry in the interstellar medium (Bacchus-Montabonel and Talbi 2008; Chenel et al. 2010).

2 Radiative association

2.1 Theoretical treatment

As far as no low-lying excited electronic states could be accessible, the mechanism for radiative association involves the formation of a complex considered to exist in the vibration quasi-continuum of the ground electronic state, which stabilizes by radiating energy to the bound rovibrational levels through spontaneous emission: $A + B \rightarrow AB^* \rightarrow AB + h\nu$.

The quantum form of the corresponding cross section at a given relative collision energy E of the colliding species is thus given by:

$\sigma(E) = \sum_J \sigma_J(E)$ with

$\sigma_J(E) = \sum_{v'J'} \frac{64}{3} \frac{\pi^5}{c^3} \frac{g}{2\mu E} v_{E,v'J'}^3 S_{JJ'} M_{EJ,v'J'}^2$

where μ is the reduced mass, g a parameter corresponding to the statistical weight of the potential energy curve, and $S_{JJ'}$ stands for the Hönl-London coefficient. The emitted photon frequency $v_{E,v'J'}$ corresponds to the energy difference between the continuum level of energy E and the rovibrational bound states, $\Delta E = h v_{v'J'} = E - E_{v'J'}$.

The expression involves the determination of the free-bound transition moment matrix elements $M_{EJ,v'J'}^2$ of the dipole moment $D(R)$ between the energy-normalized continuum function f_{EJ} and the bound rovibrational functions $\varphi_{v'J'}$ of the corresponding potential:

$$M_{EJ,v'J'} = \int_0^\infty f_{EJ}(R)D(R)\phi_{v'J'}(R)\mathrm{d}R.$$

The rate constants $k(T = \langle v\sigma \rangle$ are calculated by averaging the cross sections $\sigma(E)$ over a Maxwellian velocity distribution at temperature T:

$$k(T) = \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty E\sigma(E) \exp(-E/k_B T)\mathrm{d}E$$

Such approach leads to accurate results for the formation of diatomic molecules, as shown for example for the formation of LiH in the early universe (Gianturco and Gori-Giorgi 1997; Dalgarno et al. 1996). It can be extended with a good accuracy for more complex systems involving the formation of polyatomic species. We have studied, in particular, the $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$ radiative association process (Bacchus-Montabonel et al. 2000) for which

Table 1 Radiative association rate constants for the formation of LiH (in 10^{-20} cm^{3}s^{-1})

T (K)	Semi-classical treatment	Quantal treatment	
		Dalgarno et al. (1996)	Gianturco and Gori-Giorgi (1997)
400	3.13	3.11	2.40
500	2.84	2.94	2.28
1,000	2.15	2.08	1.66
1,500	1.80	1.51	1.22
2,000	1.57	1.15	0.93
5,000	1.00	0.40	0.33

experimental data are available (Gerlich and Kaefer 1989) and may be compared positively with theoretical values.

A simpler expression may, however, be derived in the semi-classical scheme, the radiative association cross sections, averaged over all values of the collision energy E and impact parameter b, being then determined from the transition probability for spontaneous emission $A(R)$ taking account, as previously, of the probability g that the two species approaching each other from their ground state do yield to the electronic ground state of the molecule:
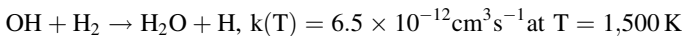
$$\sigma(E) = 2\pi g \left(\frac{\mu}{2E}\right)^{1/2} \int_0^\infty b\,\mathrm{d}b \int_{R_C}^\infty A(R) \times \left(1 - \frac{b^2}{R^2} - \frac{U(R)}{E}\right)^{-1/2} \mathrm{d}R$$

where $U(R)$ is the ground state potential energy curve.

Such approach may be compared quite positively with the quantal treatment, as shown in Table 1 for the formation of LiH (Bacchus-Montabonel and Talbi 1999; 2007). The values appear a bit overestimated with regard to the quantal ones, but the good order of magnitude is achieved with a very simple treatment. This provides a rapid and nevertheless efficient method which could be particularly interesting for the study of the formation of complex species.

2.2 Formation of H₂O by radiative association from O and H₂

Astrophysical observations have revealed the presence of water molecules in the atmospheres of evolved stars in the high temperature regions (1,500–3,000 K) with controversial abundances and distributions (Ryde et al. 2006). It is important to understand how these molecules could be formed from gas phase chemistry. The possible processes in these environments are mostly neutral–neutral reactions involving H₂ and OH:

$$\mathrm{OH} + \mathrm{H_2} \rightarrow \mathrm{H_2O} + \mathrm{H}, \quad k(T) = 6.5 \times 10^{-12}\,\mathrm{cm^3s^{-1}}\,\text{at } T = 1{,}500\,\mathrm{K}$$

(Isaacson 2008)

Another process that might contribute to the formation of water in such regions is radiative association. The rate constant for the OH + H → H₂O + hν reaction is a strongly decreasing function of temperature, very small in warm regions, $k(T) = 2.8 \times 10^{-21}$ cm^{3}s^{-1} at $T = 300$ K (Smith 1989). Such process could be relevant for cool atomic H regions, but not in the present warm atmospheres. The formation of H₂O from the radiative association of O and H₂ has thus been proposed (Glassgold et al. 2009) as a possible source of water. The reaction being not yet discussed in the literature, we have calculated the O + H₂ → H₂O + hν rate constants, in particular at high temperatures. As the process is occurring in the high atmosphere of stars, atomic oxygen has been considered both in its ground ³P and excited ¹D state.
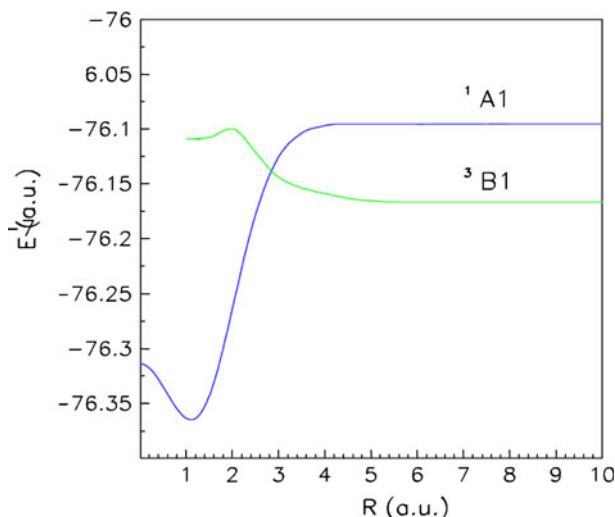
Fig. 1 $H_2O(^1A_1)$ and $H_2O(^3B_1)$ minimum energy surfaces calculated in C_{2v} symmetry as a function of the distance between O and the middle of the H_2 bound

The molecular calculations have been carried out at the CASSCF–MRCI level of theory using the MOLPRO suite of ab initio programs (Werner and Knowles 2009) and employing the correlation-consistent aug-cc-pV5Z basis sets of Woon and Dunning (1993). The calculation has been performed in the C_{2v} symmetry and the H–H coordinate has been optimized all along the path. The potential energy curves for the $^1A_1$ state corresponding to the $O(^1D) + H_2$ reaction path and the $^3B_1$ one corresponding to $O(^3P) + H_2$ are presented in Fig. 1. The crossing point has been located using diffuse atomic orbitals to accommodate the Rydberg character of the $^3B_1$ state. It corresponds to a distance of approach of 2.85 a.u. (OH = 2.95 a.u.) and an HH bond distance of 1.56 a.u. (HOH = 30.6°) and lays at 0.78 eV above the $O(^3P) + H_2$ limit.

No activation barrier is observed along the $O(^1D) + H_2$ path, in agreement with previous theoretical work (Schatz et al. 1997). Anyway, in the semi-classical scheme, the corresponding rate constants are strongly decreasing with temperature, reaching $k(T) = 1.4 \times 10^{-19}$ cm^3s^{-1} at $T = 300$ K and $k(T) = 6.2 \times 10^{-20}$ cm^3s^{-1} at $T = 1,500$ K. Such values are far too small for this radiative association process to be competitive with other formation processes as for example the $OH + H_2 \rightarrow H_2O + H$ reaction. The situation is even worse for the $O(^3P) + H_2$ reaction path. The potential energy curve presents in that case an energy barrier in the entrance channel. The efficiency of the formation of H_2O ($^1A_1$) will thus depend on the height of this activation energy barrier and also on the strength of the spin orbit coupling to pass from the H_2O ($^3B_1$) to the H_2O ($^1A_1$) surface. From these results, it appears clearly that the radiative association of O and H_2 is not an efficient process for the formation of H_2O at high temperatures.

3 Charge transfer processes

3.1 Theoretical approach

The single charge transfer process $A^{q+} + B \rightarrow A^{*(q-1)+} + B^+$ may be treated in the framework of the molecular description of the collisions. We have thus to determine the

potential energies of the different molecular states involved in the process as well as the couplings between these states. They are determined by means of ab initio quantum chemistry calculations. The process being driven mainly by the non-adiabatic interactions in the vicinity of avoided crossings (Lasorne et al. 2004), the corresponding radial coupling matrix elements between all pairs of states of the same symmetry are calculated by means of the finite difference technique:

$$g_{KL}(R) = \langle \psi_K | \partial/\partial R | \psi_L \rangle = \lim_{\Delta \to 0} \frac{1}{\Delta} \langle \psi_K(R) | \psi_L(R + \Delta) \rangle.$$

The value $\Delta = 0.0012$ a.u. previously tested (Bacchus-Montabonel et al. 1991) is generally adopted for the parameter Δ. For higher collision energies in the keV range, the rotational coupling $\langle \psi_K | iL_y | \psi_L \rangle$ between states corresponding to $\Delta\Lambda = \pm 1$ has also to be considered. It is determined directly from the quadrupole moment tensor which allows the consideration of translation effects in the collision dynamics (Fraija et al. 1994).

Using these molecular data, a collision treatment has to be carried out in order to determine the charge transfer cross sections. The rate coefficients are then calculated, as stated in previous paragraph, by averaging the cross sections over a Maxwellian velocity distribution at temperature T. The choice of the collision method depends on the collision energy range. For low energy collisions, in the eV range, which occur in the interstellar medium, quantum approaches are necessary to take into account the trajectory effects. Time-independent approaches using partial wave decomposition may provide cross sections with a good accuracy (Gargaud et al. 1993) in a wide collision range. A more physical insight is exhibited by means of time-dependent quantum dynamics using partial wave propagation methods (Baloïtcha et al. 2001). They are, however, harder to handle at very low energies and may be restricted rather in the 1–10 eV range. For higher collision energies, typically in the keV region, the collision dynamics is more likely treated by semi-classical approaches considering a rectilinear trajectory for the nucleus, in particular the EIKONXS program based on an efficient propagation method (Allan et al. 1990).

3.2 Charge transfer in the $C^+ + S$ collision system

The $C^+ + S$ charge transfer reaction and its reverse process play a determinant role in the formation of sulphur molecules in space. It is crucial in the chemistry of the photon-dominated regions (PDR's) of the interstellar medium (Teyssier et al. 2004) and allows the enhancement of the ionic carbon chemistry at the origin of the formation of the complex carbon molecules observed in the PDR's. The rate constant generally accepted for this process is 1.5×10^{-9} cm^{3}s^{-1} (UMIST database) between 10 and 41,000 K, but it appears uncertain for such a large temperature domain and accurate calculations are necessary.

At low temperatures where the process takes place, the different species may be in their ground state. With regard to the correlation diagram, only two molecular states $\{C^+(2s^22p)^2P + S(3s^23p^4)^3P\}$ and $\{C(2s^22p^2)^3P + S^+(3s^23p^3)^4S\}$ have to be considered in the direct charge transfer reaction for the doublet manifold. However, the higher $\{C(2s^22p^2)^1D + S^+(3s^23p^3)^4S\}$ configuration is close in energy with the entry channel and has to be considered for the quartet states.
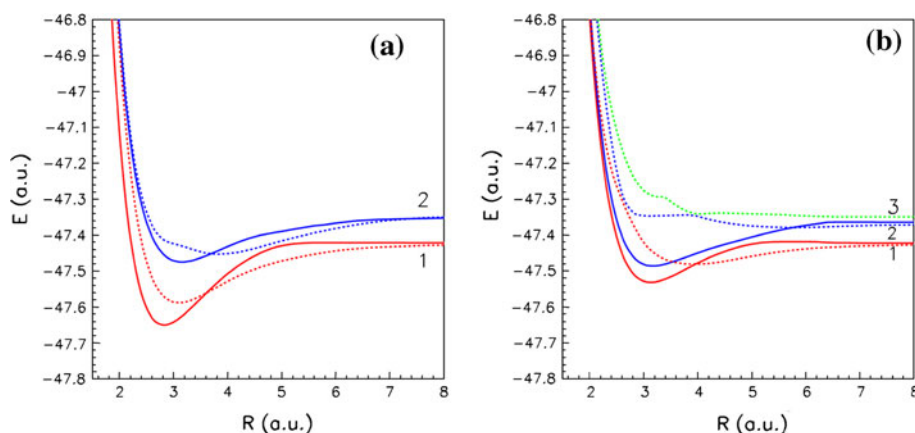
Fig. 2 **a** Adiabatic potential energy curves for the Σ (*full lines*) and Π (*dashed lines*) states of the doublet manifold of the CS^+ molecular system. (*1*) $\{C(2s^22p^2)^3P + S^+(3s^23p^3)^4S\}$. (*2*) $\{C+(2s^22p)^2P + S(3s^23p^4)^3P\}$ entry channel. **b** Adiabatic potential energy curves for the Σ (*full lines*) and Π (*dashed lines*) states of the quartet manifold of the CS^+ molecular system. *1* and *2*, same labels as in Fig. 3a. *3* $\{C(2s^22p^2)^1D + S^+(3s^23p^3)^4S\}$

Correlation diagram

| Configuration	Molecular states	Asymptotic energy (eV) (NIST database)
$C(2s^22p^2)^1D + S^+(3s^23p^3)^4S$	$^4\Sigma, \ ^4\Pi, \ ^4\Delta$	1.26
$C^+(2s^22p)^2P + S(3s^23p^4)^3P$	$^{2,4}\Sigma, \ ^{2,4}\Pi, \ ^{2,4}\Delta$	0.92
$C(2s^22p^2)^3P + S^+(3s^23p^3)^4S$	$^{2,4,6}\Sigma, \ ^{2,4,6}\Pi$	0.0

The calculations have been performed at the state-average CASSCF–MRCI level of theory using the MOLPRO code (Werner and Knowles 2009). The ECP10sdf relativistic pseudo-potential has been used to describe the 10 core-electrons of sulphur (Nicklass et al. 1995) with the correlation-consistent aug-cc-pVQZ basis sets of Dunning for all atoms (Woon and Dunning 1993). The potential energy curves are presented in Fig. 2a, b for doublet and quartet manifolds. The $^2\Sigma$ and $^2\Pi$ potentials show a smooth avoided crossing around $R = 5$ a.u., in agreement with previous calculations (Larsson 1985; Honjou 2008). For the quartet manifold, a similar smooth avoided crossing is observed for the $^4\Sigma$ potential energy curves. But a strong interaction between the $^4\Pi$ entry channel and the upper $^4\Pi\{C(2s^22p^2)^1D + S^+(3s^23p^3)^4S\}$ level is exhibited around $R = 4$ a.u. which is determinant in the description of the process.

The collision dynamics has been performed using both semi-classical and quantal wave packet methods and an analysis of both approaches has been developed (Chenel et al. 2010). As spin–orbit effects may be neglected in the collision energy range of interest, calculations have been performed separately for doublet and quartet manifolds. With consideration of statistical weights between Σ and Π states, the cross sections for doublet and quartet manifolds are expressed from the cross sections σ^Σ and σ^Π for Σ and Π states, respectively $^{2,4}\sigma = \frac{1}{3}\sigma^\Sigma + \frac{2}{3}\sigma^\Pi$, and the total cross section is then $\sigma_{tot} = \frac{1}{3}\,^2\sigma + \frac{2}{3}\,^4\sigma$ with regard to the statistical weights between doublet and quartet manifolds. The cross sections

for the direct reaction $C^+(2s^22p)^2P + S(3s^23p^4)^3P \rightarrow C(2s^22p^2)^3P + S^+(3s^23p^3)^4S$ are presented in Fig. 3. The quartet states provide the main contribution to the total cross section at low collision energies and the consideration of the upper $^4\Pi\{C(2s^22p^2)^1D + S^+(3s^23p^3)^4S\}$ level is necessary for an accurate description of the system. The semiclassical partial cross sections for the doublet manifold are in excellent agreement with the quantal wave packet approach for collision energies higher than 8–10 eV. This is a very interesting result as it allows the use of semiclassical approaches far below the generally accepted domain of accuracy. As expected, of course, the quantal calculation deviates at lower energies from the semiclassical one. The variation is less sensitive for the quartet cross sections; the wave packet values remain always close to the previous semiclassical ones, even at energies down to 1 eV. As the quartet manifold corresponds to a statistical weight two times higher than the doublet one, the total cross sections remain close in wave packet and semiclassical approaches, even at energies low with regard to the domain of validity of the semiclassical method. Such a result is very encouraging to have, at low price, an order of magnitude of cross sections, and consequently rate coefficients, for a number of astrophysical processes.

This may be visualized on the corresponding rate constants presented in Table 2 using, on one hand, the semi-classical cross sections, and, on the other hand, the wave packet quantal approach in the 0.5–10 eV collision range, completed by the semiclassical values at higher collision energies. The difference between semiclassical and quantal wave packet rate coefficients is relatively small with a relative error bar about 10–20% for most temperatures. The absolute values are significantly lower than the suggested one 1.5×10^{-9} cm^{3}s^{-1} given in the UMIST data base for the 10–41,000 K temperature range. However, a smooth variation of the calculated rate constants is exhibited in a wide temperature domain and a mean value of about $1. \times 10^{-10}$ cm^{3}s^{-1} could be assumed in the 5,000–50,000 K temperature range with a reasonable accuracy. This result is in accordance
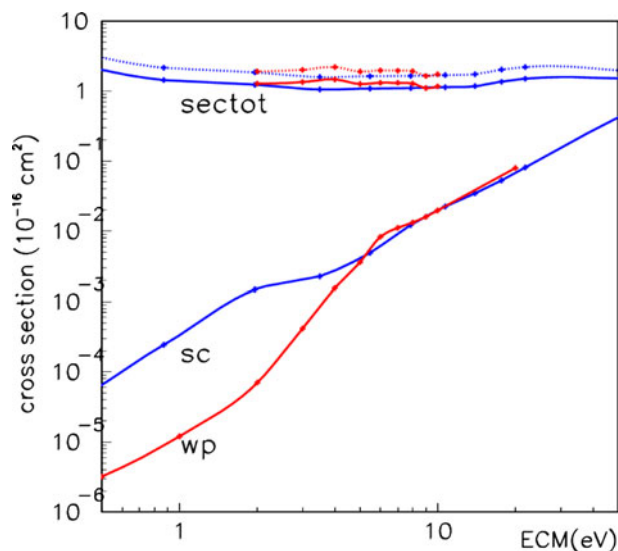
Fig. 3 Semiclassical (*blue*) and wave packet (*red*) partial and total cross sections for the CS$^+$ molecular system in the 0.5–50 eV ECM energy range: doublet manifold (*solid line*), quartet manifold (*dotted line*), total cross section (*solid line*) (color figure online)

Table 2 Rate coefficients for the $C^+ + S$ reaction (in $cm^3 s^{-1}$)

T (K)	$C^+(^2P) + S(^3P) \rightarrow C(^3P) + S^+(^4S)$	
	Semi-classic	Wave packet
500	1.8×10^{-11}	1.3×10^{-11}
1,000	3.8×10^{-11}	3.7×10^{-11}
5,000	7.3×10^{-11}	8.7×10^{-11}
10,000	7.3×10^{-11}	1.0×10^{-10}
50,000	1.3×10^{-10}	1.5×10^{-10}

with the constant rate coefficient considered in astrophysical models; the usual value seems to be overestimated by about a power of 10.

References

Allan RJ, Courbin C, Salas P, Wahnon P (1990) State-selective effects in the differential cross section for electron capture from laser-excited sodium atoms by protons. J Phys B 23:L461–L466

Bacchus-Montabonel MC, Talbi D (1999) A theoretical treatment of the LiH and BeH formation through radiative association. J Mol Struct THEOCHEM 463:91–97

Bacchus-Montabonel MC, Talbi D (2007) Isotopic effect in LiD and BeD formation through radiative association. AIP Conference Proceedings 935:170–175

Bacchus-Montabonel MC, Talbi D (2008) Ab initio treatment of charge transfer in CS^+ molecular system. Chem Phys Lett 467:28–31

Bacchus-Montabonel MC, Courbin C, McCarroll R (1991) State-selective electron capture by O^{2+} from He. J Phys B 24:4409–4417

Bacchus-Montabonel MC, Talbi D, Persico M (2000) Quantum chemical determination of the rate coefficients for radiative association of CH_3^+ and H_2. J Phys B 33:955–959

Baloïtcha E, Desouter-Lecomte M, Bacchus-Montabonel MC, Vaeck N (2001) Wave packet methods for charge exchange processes in ion-atom collisions. J Chem Phys 114:8741–8751

Chenel A, Mangaud E, Justum Y, Talbi D, Bacchus-Montabonel MC, Desouter-Lecomte M (2010) Quantum dynamics of the charge transfer in $C^+ + S$ at low collision energies. J Phys B 43:245701

Dalgarno A, Kirby K, Stancil PC (1996) The radiative association of Li^+ and H, Li and H^+, and Li and H. Astrophys J 458:397

Dubrovich VK (1977) Prospects for determining the primordial abundances in the universe. Soviet Astr Lett 3:181–182

Fraija F, Allouche AR, Bacchus-Montabonel MC (1994) Ab initio treatment of electron capture by B^{4+} ions from atomic hydrogen. Phys Rev A 49:272–276

Gargaud M, Bacchus-Montabonel MC, McCarroll R (1993) Charge transfer of O^{2+} in helium at thermal and low eV energies. J Chem Phys 99:4495–4499

Gerlich D, Kaefer G (1989) Ion trap studies of association processes in collisions of CH_3^+ and CD_3^+ with n-H_2, p-H_2, D_2, and He at 80 K. Astrophys J 347:849–854

Gianturco FA, Gori-Giorgi P (1997) Radiative association rates and structure of resonances for Li and Li^+ colliding with H and H^+. Astrophys J 479:560–567

Glassgold AE, Meijerink R, Najita JR (2009) Formation of water in the warm atmospheres of protoplanetary disks. Astrophys J 701:142–153

Honjou N (2008) Ab initio study of molecular vibrations in the $X^2\Sigma^+$, $A^2\Pi$, and $C^2\Sigma^+$ states of CS^+ and the vibrational structure in the photoelectron spectrum of CS. Chem Phys 344:128–134

Honvault P, Gargaud M, Bacchus-Montabonel MC, McCarroll R (1995) Recombination of O^{2+} ions by electron capture from atomic hydrogen in photo-ionized nebulae. Astron Astrophys 302:931–934

Isaacson AD (2008) Including anharmonicity in the calculation of rate constants II. The $OH + H_2 \rightarrow H_2O + H$ reaction. J Chem Phys 128:134304

Larsson M (1985) Ab initio potential curves and electronic transition moments of CS^+. Chem Phys Lett 117:331–335

Lasorne B, Bacchus-Montabonel MC, Vaeck N, Desouter-Lecomte M (2004) Nonadiabatic interactions in wave packet dynamics of the bromacetyl chloride photodissociation. J Chem Phys 120:1271–1278

Nicklass A, Dolg M, Stoll H, Preuss H (1995) Ab initio energy-adjusted pseudopotentials for the noble gases Ne through Xe: Calculation of atomic dipole and quadrupole polarizabilities. J Chem Phys 102:8942–8952

NIST Atomic Spectra Database Levels. http://www.physics.nist.gov/cgi-bin/AtData:main_asd

Ryde N, Harper GM, Richter MJ, Greathouse TK, Lacy JH (2006) Water vapour on Betelgeuse as revealed by TEXES high-resolution 12 μm spectra. Astrophys J 637:1040–1055

Schatz GC, Papaioannou A, Pederson LA, Harding LB, Hollebeek T, Ho T-S, Rabitz H (1997) A global A-state potential surface for H_2O: influence of excited states on the $O(^1D) + H_2$ reaction. J Chem Phys 107:2340–2350

Smith IWM (1989) Radiative association in collisions between neutral free radicals. Chem Phys 131:391–401

Talbi D, Bacchus-Montabonel MC (2010) The formation of H_2O from the radiative association of O and H_2. Chem Phys Lett 458:56–58

Teyssier D, Fossé D, Gerin M, Pety J, Abergel A, Roueff E (2004) Carbon budget and carbon chemistry in proton dominated regions. Astron Astrophys 417:135–149

The UMIST database for Astrochemistry. http://www.udfa.net

Vaeck N, Bacchus-Montabonel MC, Baloïtcha E, Desouter-Lecomte M (2001) Time dependent wave packet treatment of the $Si^{4+} + He$ collision. Phys Rev A 63:042704

Werner HJ, Knowles P (2009) MOLPRO package of ab initio programs (version 2009.1)

Woon DE, Dunning TH Jr (1993) Gaussian basis sets for use in correlated molecular calculations. J Chem Phys 98:1358–1371