

Hot-atom Chemiluminescence: A Beam Study of the $O(^3P) + H_2, CH_4$ Systems

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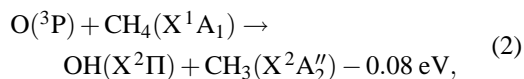
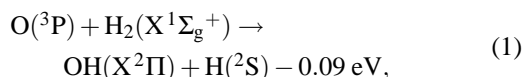
Z. Naturforsch. **59a**, 517–522 (2004); received March 1, 2004

A beam of fast oxygen atoms in the $O(^3P)$ state was collided with H_2 and CH_4 at 10–300 eV_{lab}. Chemiluminescence spectra for the H_2 target show $OH(A-X)$ emission, while for the CH_4 target $OH(A-X)$ as well as $CH(A,B-X)$ emissions are observed. Excitation functions were obtained. For the H_2 target they resemble those of $N(^4S) + H_2$ collisions, while for the methane target the $OH(A)$ yield increases with collision energy up to 50 eV_{CM} and later decreases slowly, according to the “billiard ball” model.

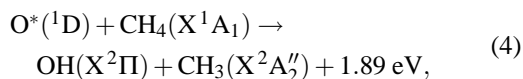
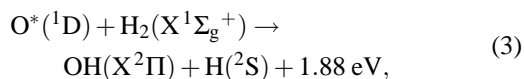
Key words: Chemiluminescence; Energy Transfer; Chemical Reactions; Hot Atoms; Oxygen.

1. Introduction

Reactions of atomic oxygen with hydrogen and methane are important in atmospheric chemistry and combustion. The reactions of ground state oxygen, $O(^3P)$, are asymptotically slightly endothermic to give the ground state OH product:

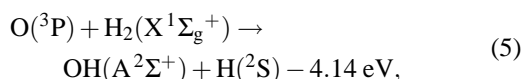


(the energy balance for all equations throughout this work is based on data taken from [1–4]). Both reactions have a barrier of ~ 0.5 eV [5, 6]. Experimental studies of these systems are rather difficult, involving in the past techniques such as flash photolysis-shock tube, flow tube, and laser photolysis with laser-induced fluorescence; details for $O(^3P) + H_2$ and $O(^3P) + CH_4$ reactions can be found, e. g., in [7–10] and [11–14], respectively (see also references therein). All experimental studies have a problem with the elimination of undesired contributions from the exothermic reactions of oxygen atoms in the lowest metastable state:

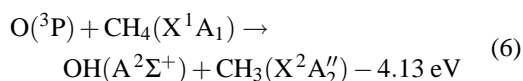


which occur much faster (in [15] it is estimated that at a collision energy of 0.5 eV the cross section for the reaction (3) is one million times larger than that for (1)). Many important results are derived from theoretical studies (too numerous to be listed here, for reaction (1) see e.g. [15, 16], for reaction (2) see e.g. [6, 17–20] and references therein). It is now generally accepted that both reactions proceed mainly via the abstraction mechanism.

In the present work we study reactions analogous to (1) and (2), but leading to electronically excited products. The chemiluminescence studies of the processes

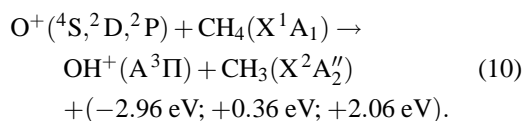
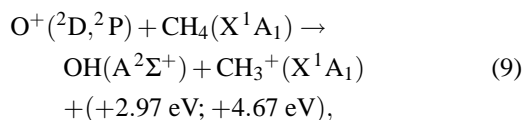
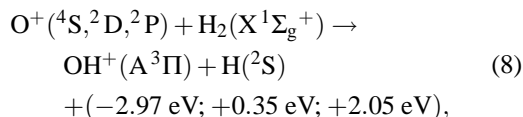
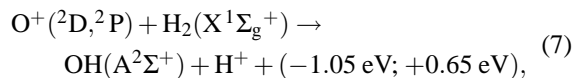


and



must be performed at hyperthermal collision energies to satisfy energy requirements. For this reason we use an ionic beam containing mainly $O^+(^4S)$ ions with specified kinetic energy; the beam is transformed by charge exchange with a suitable gas to a neutral

O(³P) beam of the same kinetic energy. The studies are closely related to their ionic counterparts:



The energy values in parentheses at the end of (7)–(10) give energy balances for the reactions of oxygen ion in electronic states specified on the left side, that is ground state O⁺(⁴S), the lowest metastable state O⁺(²D) at 3.32 eV above the ground state, and the second lowest metastable state O⁺(²P) at 5.02 eV, respectively. The O⁺(⁴S) ion is not considered in (7) and (9) because the rule of conservation of the overall spin is generally obeyed in ionic chemiluminescent reactions [21].

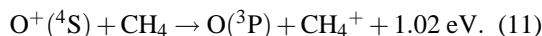
Chemiluminescence was observed in the past for the O⁺ + H₂ [22, 23] and O⁺ + CH₄ [23] reactions, and the emissions had to be attributed to the reactions of oxygen ions in metastable states. The results obtained here for the ionic reactions serve mainly for the estimation of an undesired (but possible) metastable content of the neutral beam. In the present work we tried to minimize the metastable fraction in the ion beam, to obtain the neutral beam of O(³P) only. The experimental method applied here is the same as in our previous work with hot atoms [24–28].

2. Experimental

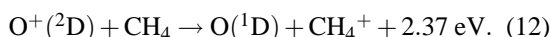
The experimental set-up consists of a Colutron-type ion source, a mass spectrometer, a neutralization cell, a reaction cell, and a spectroscopic photon detection system. Oxygen ions were generated from CO at an ion source pressure of ~25 Pa and an anode-to-cathode voltage $U_A = 34$ V, the lowest possible for a reliable measurement of the ion beam current at low energies.

The ions were extracted from the source, mass analyzed at 1000 eV_{lab}, and subsequently decelerated to the desired energy. The energy range used was 10–300 eV_{lab}, with corresponding ion currents of 0.1–1 nA. At the low value of U_A used, the ion beam current was weak indeed, about an order of magnitude lower than when U_A was set to 88 V. Nevertheless, the unusual conditions of the beam source were applied to minimize the production of metastable excited states of oxygen ions. These states are known to be formed efficiently in the ion beam source when $U_A > 35$ V [23]. In some experimental runs U_A was deliberately set to 88 V (“high metastable-ion content” regime, to compare the observations with the results of [23], where this value of U_A was used), and even to a higher value of $U_A = 110$ V. We found that the experimental conditions corresponding to a high metastable beam content lead to similar results as in Figs. 16, 17 of [23]. Despite our efforts, the experimental results described below suggest that we still had some metastable ions present in the O⁺ beam.

In the neutralization cell the O⁺ ion beam was converted into a beam of oxygen atoms of the same energy in a near-resonant charge transfer reaction. Noble gases (Kr, Xe) were tried, but in the end methane was used as the neutralizing gas, acting according to the scheme



Although not in perfect resonance, this process is exothermic and the polyatomic cation is capable of absorbing excess energy. The contamination of the O⁺(⁴S) ion beam e.g. by the metastable O⁺(²D) ions could lead to the formation of fast metastable O(¹D) atoms:



The pressure of the neutralizing gas was 15 Pa in all experiments, causing an ion beam attenuation of about 60%. The residual ions were prevented from entering the reaction cell by applying a repelling voltage of 100–400 V. The spectra were recorded with a 1024-channel optical detector coupled with a McPherson 218 spectrograph, which was equipped with a 300 l/mm grating blazed at 500 nm, allowing for simultaneous accumulation over a 196 nm spectral range. At a target gas pressure of 2 Pa (measured with a capacitance manometer) and a 1.5 mm wide monochromator entrance slit (spectral resolution: 12 nm FWHM), the

chemiluminescence signal (integrated over all detector channels) was between 0.5 and 15 cts/s, depending on the target gas and the collision energy. The detector dark count rate was 2 cts/s. All spectra were loaded in a computer, smoothed over 7 channels and corrected for spectral response; later they were processed to obtain integrated intensities of the molecular bands observed, for the determination of excitation functions.

3. Results and Discussion

An exemplary chemiluminescence spectrum obtained for $O(^3P) + H_2$ at a kinetic energy well above the thermodynamic threshold is shown in Fig. 1a. It can be compared with the chemiluminescence spectrum at the same collision energy for $O^+ + H_2$ (Fig. 1c). Both spectra were recorded in succession, with all experimental conditions identical, except that the neutralization cell was first filled with CH_4 and later emptied. The spectrum in Fig. 1a is identified as due to the $OH(A^2\Sigma^+ - X^2\Pi)$ transition [29], with clearly distin-

guishable $\Delta v = 0$ and $\Delta v = +1$ sequences. In the spectrum of Fig. 1c the $OH(A-X)$ emission is somewhat obscured by the underlying $OH^+(A^3\Pi - X^3\Sigma^-)$ broad band chemiluminescence, presented already in [22]. The peak at 395 nm in Fig. 1c is most probably associated with atomic transitions in oxygen. A group of five lines, belonging to the $4p^5P_J - 3s^5S_2$ and $3s^3P_J^o - 3p^3P_J$ transitions in neutral oxygen, is known to appear in this region [30, 31]. The upper levels have energies of 12.28 eV and 14.12 eV, respectively, and, for the reason of energy balance, the lines must arise from the charge exchange between metastable oxygen ions and H_2 (the ionization potentials of oxygen atom and hydrogen molecule are equal to 13.62 eV and 15.43 eV, respectively [3]). Below the spectra in Figs. 1a, c, another pair of spectra is shown (Fig. 1b, d), for lower collision energies. One can see that the $OH(A-X)$ emission almost vanishes for the $O(^3P)$ reaction (Fig. 1b), and for the O^+ reaction (Fig. 1d) it is weaker and hard to distinguish from $OH^+(A-X)$, which has the $\Delta v = +2$ sequence in the same spectral region. It seems that the disappearance of the $OH(A-X)$, $\Delta v = +1$ sequence in Fig. 1d indicates that the neutral emission is much weaker than the $OH^+(A-X)$ chemiluminescence at this collision energy.

Figure 2a presents the luminescence spectrum recorded for $O(^3P) + CH_4$ at relatively high collision energy, to be compared with the spectrum for $O^+(^4S) + CH_4$ at the same energy (Fig. 2c). Both spectra contain bands belonging to the $CH(A^2\Delta, B^2\Sigma^- - X^2\Pi)$ transitions and look quite similar, except that for the ionic system there is a weak signal of the $\Delta v = 0$ sequence of the $OH^+(A^3\Pi - X^3\Sigma^-)$ transition. In Fig. 2b, c the spectra for the same systems, recorded at much lower energy, are presented. Here a major difference is observed: for the neutral system the $CH(A, B-X)$ emissions are still visible (although they appear slightly changed, with a somewhat broadened maximum), while for the ionic system they are virtually absent. This difference suggests some contribution of the $O(^1D)$ reactions. A much stronger effect of this kind was observed for the $N + CH_4$ system [28], when the luminescence from $N(^4S) + CH_4$ and $N(^2D) + CH_4$ was compared. Although the $N + CH_4$ system is not isoelectronic with the one studied here, it is nevertheless believed to behave analogously when it comes to reaction dynamics of the metastable D-state [32]. For the $N + CH_4$ system, very efficient formation of $CH(A, B)$ at energies below 40 eV_{CM} was found to be a signature of the reaction of fast metastable $N(^2D)$

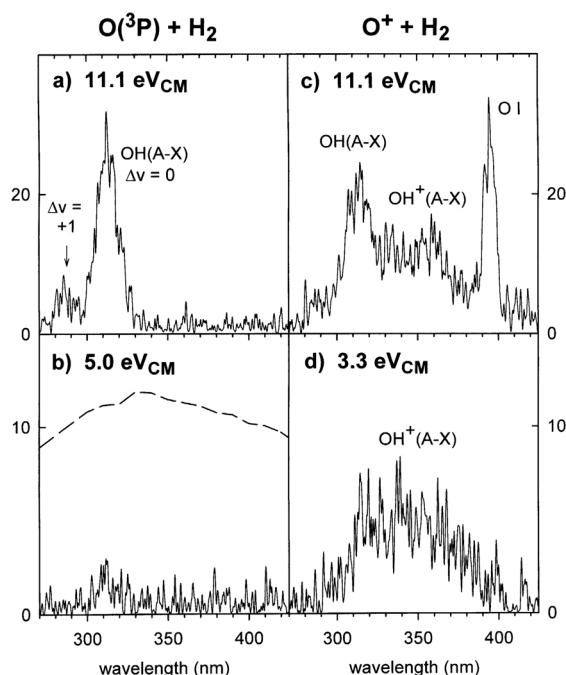


Fig. 1. Chemiluminescence spectra from $O(^3P) + H_2$ (panels a and b) and $O^+ + H_2$ collisions (panels c and d) at the collision energies indicated above. Spectral resolution: 12 nm FWHM. The group of neutral oxygen O I lines around 395 nm is identified in the text. The spectra are not corrected for the relative spectral response of the detection system, which is given by the dashed line in panel (b).

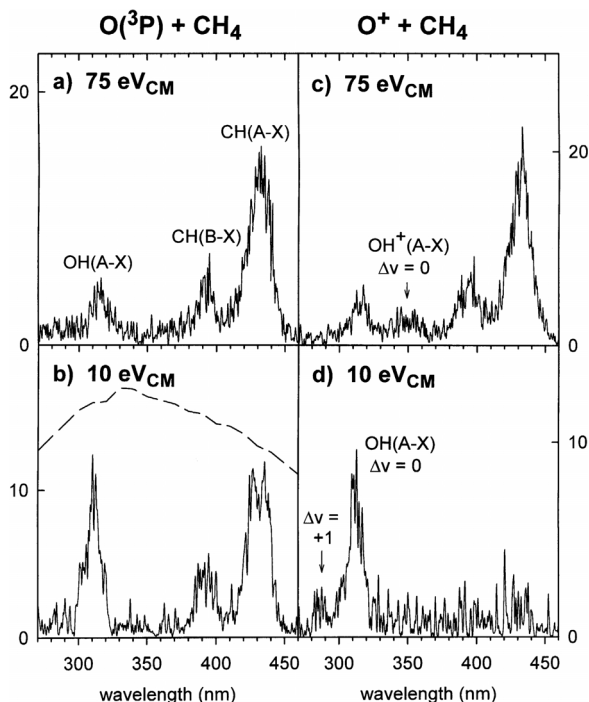


Fig. 2. A comparison of the luminescence spectra for $O(^3P) + CH_4$ (panels a and b) and $O^+ + CH_4$ (panels c and d), at the collision energies indicated above. Spectral resolution: 12 nm FWHM. The spectra are shown such that the strongest features have approximately the same height in all panels and are not cross-calibrated for a direct comparison of intensities. The spectra are not corrected for the relative spectral response of the detection system, which is given in panel b.

atoms, the reaction proceeding via insertion of an N atom into the C-H bond, with subsequent dissociation of the complex, a dissociation in which $CH(A)$ -formation is the most exothermic luminescent channel. For the ground state $N(^4S)$ reactions, the $CH(A)$ -formation is improbable at low energies, as for these nitrogen atoms $CH(A)$ can be produced only in the “shattering” collisions at higher energies (see Fig. 2e of [28]).

The excitation function for the $O(^3P) + H_2$ reaction is given in Fig. 3, together with those obtained for the $O^+ + H_2$ system. The shape of the function for $OH(A)$ production from the $O(^3P) + H_2$ reaction resembles that observed before for $N(^4S) + H_2$ [25]. The $OH(A-X)$ emission does obey the thermodynamic threshold of the neutral reaction (5), with some uncertainty in the collision energy caused by the Chantry effect [33]. It is worth noting that the excitation function for the production of $OH(A)$ from the ionic reaction is quite

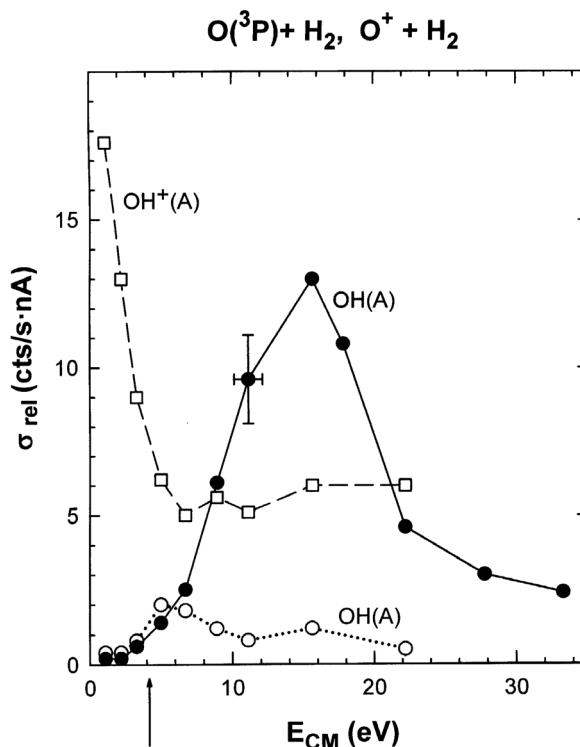
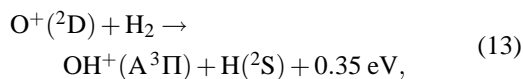


Fig. 3. Excitation functions of the $OH(A)$ product from the $O(^3P) + H_2$ collisions (dots) compared to $OH(A)$ (circles) and $OH^+(A)$ (squares) products from the $O^+ + H_2$ collisions. The thermodynamic threshold for the reaction (5) is shown by the arrow below the energy ordinate.

different from that reported in Fig. 16 of [23]. The simplest explanation of this difference lies in the fact that we apply a much lower anode voltage in the ion source, and therefore the number of ions in the lower metastable state $O^+(^2D)$ relative to those in the more energetic $O^+(^2P)$ state is higher in the present work. The shape of the excitation function for $OH^+(A-X)$ from the ionic reaction can be explained by the process



involving metastable ions. Fortunately, probably due to a larger energy mismatch in (12), than in (11), these metastable ions seem to convert less efficiently into metastable neutral atoms than it occurs in the neutralization of ground state O^+ ions into ground state oxygen atoms. There is no evidence that neutral metastables influence the excitation function for the process (5), and therefore Fig. 3 describes correctly the

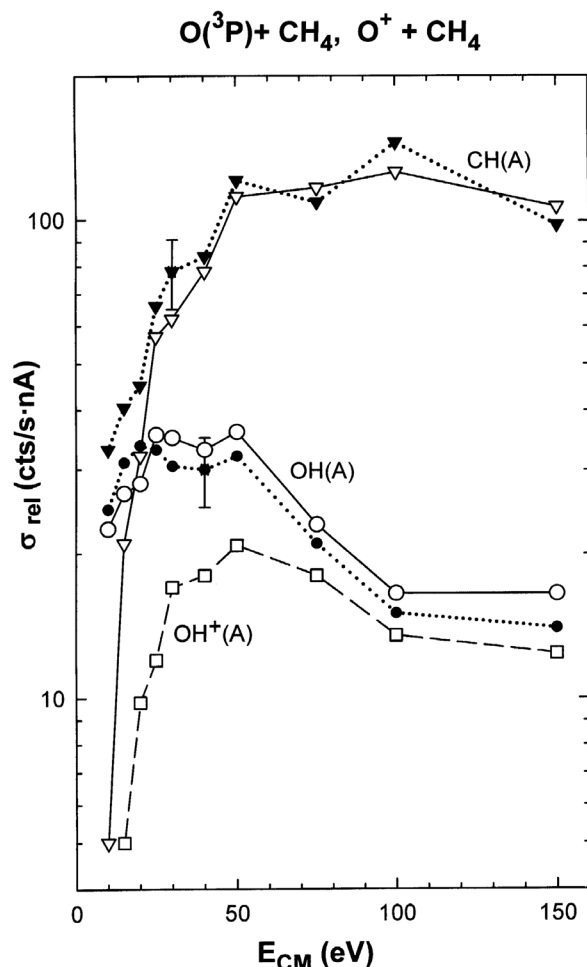


Fig. 4. Excitation functions for the $O(^3P) + CH_4$ (black symbols) and $O^+ + CH_4$ (white symbols) systems. Data points for OH(A) product are marked by circles, for CH(A) – by triangles, and for $OH^+(A)$ – by squares.

collision energy dependence for chemiluminescence from the title reaction.

Figure 4 contains the excitation functions for the $O(^3P) + CH_4$ and $O^+ + CH_4$ reactions. The cross sections for production of OH(A) are very similar for the neutral and ionic reaction, first increasing with collision energy, reaching a flat maximum at about 40 eV_{CM} and then falling-off slowly, but still being quite large at 150 eV_{CM}, where the “billiard ball” collisions [34] take place (the latter mechanism was observed also for N , $N^+ + CH_4$ [26, 28]). However, in comparison with the nitrogen reactions, an important difference occurs here: the abstraction reaction for OH(A) formation in process (6) at low en-

ergies contributes relatively less for $O(^3P)$ and O^+ reactants than in analogous nitrogen reactions. The light yield of CH(A) (CH(B) behaves identically as CH(A) and therefore is not discussed here) for neutral and ionic oxygen reactions with methane above 40 eV_{CM} is typical for the “shattering” process observed for N , $N^+ + CH_4$ (see Fig. 3 of [28]). However, below 30 eV_{CM} the CH(A) yield for the neutral system increases strongly over that of the ionic one toward lower energies, indicating a possible contribution from $O^*(^1D)$ collisions (see discussion on p. 159 of [28]). This difference in shape of the CH(A) excitation functions for the $O^+ + CH_4$ and $O + CH_4$ collisions suggests that in the present experiment the neutral beam contains a small fraction of $O(^1D)$ metastables.

The excitation functions in Figs. 3 and 4 were obtained with the same experimental parameters of the beam and of the detection system; therefore the cross sections in Figs. 3 and 4 can be compared directly. The units given have the dimension of photon counts per second per nA. The excitation functions are not corrected for the collision-energy dependence of: (i) residence times of excited products in the detection window; (ii) the effect of coulombic repulsion of ions in the ionic reactions. A precise estimate of the corrections (in particular of the latter one) is not easy to make. In [22], where a window of similar size was used, the dependence (i) was simulated and found to bring a substantial loss of light at higher laboratory energies, although the size of the effect was overestimated because the radiative lifetime of OH(A) was assumed 50% too high (1 μ s instead of 0.69 μ s recommended later in [3]). In our experiment, the inclusion of the proper correction would effectively cause some lowering of 2 or 3 data points at the lowest energies (below 50 eV_{lab}). The correction (ii) would act contrary to correction (i): the 2 or 3 points for ionic reactions at the lowest energies would be moved up in Figs. 3, 4. We tried to estimate roughly the size of the correction (ii) by comparing excitation functions obtained by us for $U_A = 88$ V (i.e. repeated after [23]) with the original ones, where this correction was made. Our estimates indicate that for the ionic reactions the two corrections should approximately cancel in our experiment, and the excitation functions presented in this work should keep their main features intact.

Acknowledgements

We thank Prof. Christoph Ottinger (Max-Planck-Institut für Strömungsforschung Göttingen, Germany)

for his encouragement and many valuable suggestions.
This work was supported by the KBN Grant No. 5
P03B 116 20.

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