Measurement of Excitation Cross-Sections for Electron Impact at low Densities of Target Atoms

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In a crossed-beam experiment Na atoms are excited by electron impact with an energy of 11 eV. Determination of the excitation cross-section for the D-lines shows an increase of the measured cross-section with decreasing particle density in the atomic beam below $10^{12}\,\mathrm{cm}^{-3}$.

The electron gun for the electron beam was similar to that described by Karstensen[1]. On its way to a photomultiplier cathode the emitted light passed a spectrograph of sufficient aperture (1 : 5). A diaphragm in the image plane of the spectrograph limited the effective interval of wavelengths from about 5500 Å to 6200 Å. For intensity reasons the spectrograph was used with an extremely wide entrance slit. A filter could be placed in the light path. Without this filter light from the 5683/88 Å doublet and the 5890/96 Å doublet reached the photomultiplier cathode. The filter absorbed all light from the D-lines. The doublets were not resolved. (Some light of the 6154/61 Å lines also passed filter and spectrograph, but had no influence on the results, as the spectral sensitivity of the photocathode for this wavelength is poor.)

As the excitation processes for the upper levels of both lines take place in the same beams, we expected the ratio of the signals due to the resonance line ($3\,^2S - 3\,^2P$, 5890/96 Å) and the non-resonance line ($3\,^2P - 4\,^2D$, 5683/88 Å) to be independent from the density of the sodium atoms for sufficient low densities. Sufficient low density means, that no appreciable diffusion of radiation by self-absorption of the resonance light occurs. We found, however, that with decreasing density of particles in the atomic beam the light of the resonance line increased relatively to the light of the non-resonance line. The density was calculated with vapour pressure data from the temperature of the furnace producing the atomic beam. Effects from residual gas in the evacuated apparatus or from erroneous zero signals could be excluded.

As the dependence of the ratio of intensities might be originated by either the $3\,^2P$ or the $4\,^2D$ level (or both), the apparatus was adapted for an absolute measurement of the excitation cross-section of the resonance doublet. The procedure was described by Schramm[2] for Calcium. (In our case the total amount of condensed sodium was determined by flame photometry.)

Figure 1 shows the result, the measured cross-section q as a function of the particle density n in the atomic beam. (The influence of self-absorption was perceptible for $n > 10^{13}\,\mathrm{cm}^{-3}$.) The plateau around $n = 10^{12}\,\mathrm{cm}^{-3}$ corresponds to $q = 42 \cdot 10^{-16}\,\mathrm{cm}^2$. This agrees reasonably well with a former value of $30 \cdot 10^{-16}\,\mathrm{cm}^2$ (Christoph[3] and Haft[4]), taking into account, that in such experiments an absolute calibration of a light sensitive device is involved. For lower densities we found a greater cross-section. Figure 1 is in agreement with the experiment described at the beginning, assuming that the signal from the non-resonance line is proportional to the particle density in the atomic beam.

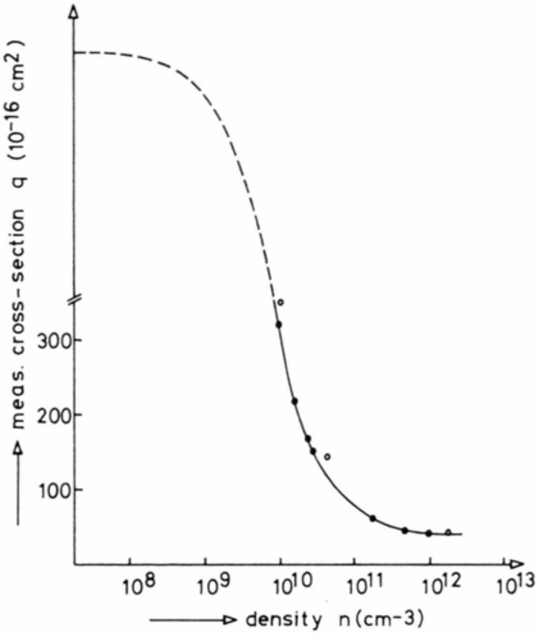

Fig. 1. Measured cross-section for Na D-lines as a function of particle density in the atomic beam.

For $n < 10^{10}\,\mathrm{cm}^{-3}$ it was not possible to derive reliable absolute cross-sections. By correlating the light intensity of the resonance lines to the particle density from the vapour pressure in the furnace, it could be shown, that for $n < 10^8\,\mathrm{cm}^{-3}$ q reaches a constant q_c (dashed line in Figure 1). As in the latter case the variation of n was much better known than n itself, the value of q_c remains uncertain.

From several different theoretical calculations follows $q = 55 - 90 \cdot 10^{-16}\,\mathrm{cm}^2$ (see Lane[5]) for 11 eV energy of the impingeing electrons. This would suggest an additional effect to be responsible for the

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increasing q with decreasing n in our experiment. At the present state of investigation no satisfying explanation can be offered. The effect is not limited to sodium, since similar results were obtained here earlier by Walter[6] and Reese[7] for the resonance line of magnesium.

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The Chemiluminescent Reaction of HCO with $O_2(^1\Delta_g)$

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A chemiluminescence spectrum above 1 μ is observed when olefins or formaldehyde are reacted with active oxygen. Part of the bands are quenched by water vapor and shifted upon deuteration of the fuel, while others are unaffected. The latter bands are attributed to the $(^2A'-^2A'')$ electronic transition of HO_2 radicals produced by the reaction of HCO radicals with $O_2(^1\Delta_g)$ metastable molecules. The quenchable bands are probably overtone transitions of vibrationally excited HO_2 radicals in the $^2A''$ ground state.

It has been proposed that metastable oxygen molecules, $O_2(^1\Delta_g)$, might contribute to the oxidation of unsaturated hydrocarbons and other atmospheric pollutants[1, 2]. However, most atmospheric trace gases deactivate $O_2(^1\Delta_g)$ extremely slowly and without chemical reaction[1, 3]. There is evidence that $O_2(^1\Delta_g)$ interacts rapidly with some radical produced by the reaction of $O(^3P)$ atoms with organic gases[4].

The free radical HCO is a common intermediate in many hydrocarbon oxidations. The reaction with ground state molecular oxygen at ambient temperature is not well known, but the rate constant is probably smaller than $10^{-15}\,cm^3\cdot molecule^{-1}\cdot s^{-1}$ (see [5]).

The present investigation was initiated by the observation of a banded spectrum above 1 μ which is emitted when active oxygen from a microwave discharge is reacted with simple olefins at low pressures. The experiments were carried out in a flow tube. The infrared spectra were recorded using a 0.6 m grating monochromator and a cooled PbS detector. Figure 1 B shows a typical infrared emission spectrum which was obtained by the reaction of ethylene (4 mtorr partial pressure) with active oxygen at 1 torr, containing both $O(^3P)$ atoms and $O_2(^1\Delta_g)$ metastable molecules. The wave numbers of the band maxima are tabulated in Table 1. Figure 1 A shows the infrared atmospheric band, in comparison, which was recorded under the same experimental conditions, but with the hydrocarbon turned off. The 1.27 μ band of the chemiluminescent spectrum is distinctly broader and more intense than the infrared atmospheric band. It was also proved that $O_2(^1\Delta_g)$ molecules are consumed in a fast reaction when the hydrocarbon is added[6]. Figure 1 C was obtained with ethylene as well, but in the presence of 0.1 torr water vapor. Under these conditions, one group of the bands was strongly quenched, while the intensity of the other group did not change appreciably. Substitution of perdeutero ethylene for ethylene resulted in spectrum Figure 1 D. Bands which are not quenched by water vapor are also not shifted by deuteration. Water-sensitive bands are shifted upon deuteration. The observations are summarized in Table 1.

Table 1. Wave numbers of prominent band maxima from the reaction of active oxygen with ethylene and perdeutero ethylene, respectively. (Bands marked with a (q) are strongly quenched by water vapor.)

$HCO+O_2(^1\Delta_g)$ Wave numbers (cm^{-1}) of band maxima	$DCO+O_2(^1\Delta_g)$ Wave numbers (cm^{-1}) of band maxima	
	not shifted	shifted
7865	7865	
6970	6975	
6599 (q)		4937
5904	5865	
5765	5765	
?		4725
4463 (q)		<4000

When active oxygen was passed over a HgO film prepared by distillation of Hg through the discharge, which removed oxygen atoms, no infrared emission was observed upon addition of ethylene, except for the infrared atmospheric band at 1.27 μ. Also, when

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$O(^3P)$ atoms were generated by NO-titration of active nitrogen and reacted with ethylene, no infrared spectrum similar to Fig. 1 B could be detected. If, however, atom-free metastable $O_2(^1\Delta_g)$ molecules from a HgO coated discharge tube were admixed below the bluish reaction zone of $O(^3P)$ atoms with ethylene, an infrared emission spectrum identical to Fig. 1 B was observed.

We conclude that the infrared spectrum Fig. 1 B is due to a reaction of $O_2(^1\Delta_g)$ with some radical from the reaction of ethylene with $O(^3P)$ atoms. It is well established that $O(^3P)$ atoms react with ethylene, producing HCO and CH_3 free radicals [7, 8]:

$$C_2H_4 + O(^3P) \rightarrow CH_3 + HCO\,. \qquad (1)$$

To distinguish between CH_3 and HCO, the two potential reaction partners of $O_2(^1\Delta_g)$ leading to infrared chemiluminescence, HCO radicals were produced from pure gaseous formaldehyde by reaction with $O(^3P)$ or fluorine atoms. $O_2(^1\Delta_g)$ from a HgO coated discharge was admixed downstream. Under such conditions, the infrared emission spectrum of Fig. 1 B was observed at higher intensity than in previous experiments with ethylene as fuel.

The experiment established that the infrared chemiluminescence spectrum, Fig. 1 B, is due to a reaction of HCO with $O_2(^1\Delta_g)$ metastable molecules. This was further confirmed by comparing infrared spectra obtained with olefins of varying structure, some of which could yield HCO radicals in a primary reaction with $O(^3P)$ atoms, while others could not.

The following exothermic reactions of HCO with $O_2(^1\Delta_g)$ have to be considered:

$$CHO + O_2(^1\Delta_g) \rightarrow CO_2 + OH; \quad \Delta H = -115 \text{ kcal/mole}; \qquad (2)$$

$$CHO + O_2(^1\Delta_g) \rightarrow HO_2 + CO; \quad \Delta H = -51 \text{ kcal/mole}\,. \qquad (3)$$

The reaction of ground state molecular oxygen with HCO at high temperatures is reported to proceed according to (3). Reaction (2) has not been observed with ground state molecular oxygen [9]. At first, reaction (2) combined with vibrational excitation of the CO_2 into the third vibrational level

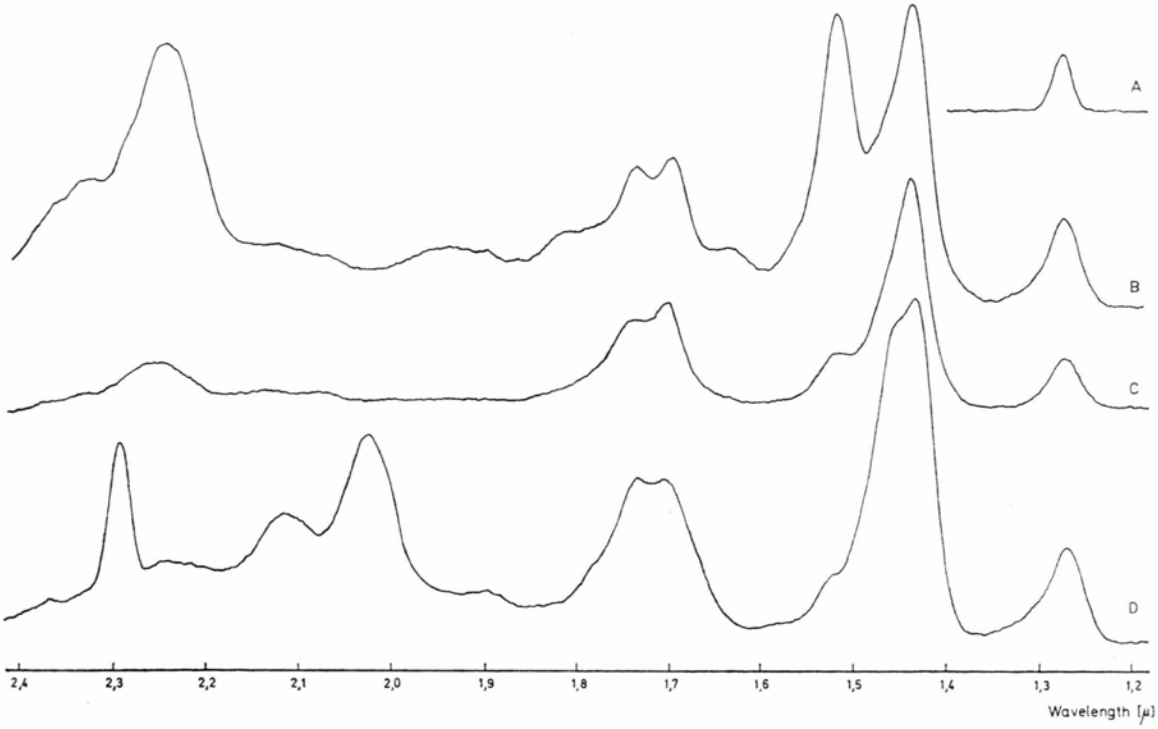

Fig. 1. Infrared chemiluminescence spectra from the reaction of active oxygen with ethylene.
A: $O_2(^1\Delta_g \rightarrow X^3\Sigma_g^-)$ atmospheric band at 1 torr active oxygen pressure,
B: chemiluminescence spectrum at 1 torr active oxygen and 4 mtorr C_2H_4,
C: as B, but with 0.10 torr H_2O vapor added downstream of the primary reaction zone,
D: as B, but with C_2D_4 as fuel. The band at 2.29 μ is the third order and the weaker band at 1.52 μ the second order of the $O_2(^1\Sigma_g^+ - ^3\Sigma_g^-)$ transition at 0.762 μ.

of the asymmetric stretching mode was considered a possibility[6]; the $(00^03)-(00^00)$ overtone band of CO_2 coincides, within experimental accuracy, with the 1.43 μ band of the observed chemiluminescence spectrum. However, several recent results disprove this identification:

(a) The 1.43 μ band does not show the typical branched structure of the CO_2 overtone band with sufficient resolution,

(b) the fundamental bands $\Delta\nu = 1$ of the asymmetric stretching mode at 4.3 μ are extremely weak at low pressures unless additional CO_2 is added to the system,

(c) the other bands of the chemiluminescence spectrum which are neither quenched by water vapor nor shifted upon deuteration cannot be identified with any of the known combination bands of CO_2. Also, no low-lying electrically excited state of CO_2 compatible with the energetics of reaction (2) has been reported.

Vibrationally and/or electronically excited HO_2 radicals from reaction (3) must therefore be considered. The vibrational frequencies of the $O-OH$ stretching vibration, $\nu_3 = 1095\ \text{cm}^{-1}$, the $H-OO$ stretching vibration, $\nu_1 = 3410\ \text{cm}^{-1}$, and the bending vibration, $\nu_2 = 1390\ \text{cm}^{-1}$ of HO_2 in its ground state have been reported in the literature[10, 11]. Overtone and combination bands of the ν_1 and ν_3 vibrational modes account, within experimental accuracy, for part of the water sensitive spectrum, and also for the shifting upon deuteration. A definitive identification cannot be given at the present time.

If the other group of emission bands which are neither shifted upon deuteration nor quenched by water vapor are also due to HO_2 radicals, only the $O-OH$ stretching vibration, $\nu_3 = 1095\ \text{cm}^{-1}$, can be involved, which is insensitive to deuteration. However, there are good reasons to exclude vibrationally excited HO_2 radicals in the electronic ground state as the emitter of these bands:

(a) The high wave numbers of these bands could only correspond to overtone transitions $\Delta\nu_3 \geqq 4$, which is extremely improbable,

(b) the spacing of the bands is not in accord with overtone transitions of a single vibrational mode.

A recent theoretical calculation has shown that the lowest electronically excited state of the HO_2 radical lies only about 17 kcal above the ground state[12]. The electronically excited state correlates with $H(^2S) + O_2(^1\Delta_g)$, while the ground state correlates with $H(^2S) + O_2(^3\Sigma_g^-)$. It is therefore reasonable to assume that electronically excited HO_2 radicals are also produced by the reaction $O_2(^1\Delta_g) + HCO$, which contains a very loosely bound H atom. This would explain why the emission spectrum includes two distinct groups of bands: One group, which we identify with the electronic transition, is not quenched by water vapor. The other group of bands, due to vibrationally excited HO_2 in its electronic ground state, is strongly quenched.

The identification of HO_2 as the emitter of the infrared chemiluminescence spectrum obtains further support by preliminary results of Hunziker et al., which were recently presented[13]. These authors investigated the gas phase absorption spectrum of the HO_2 free radical in the region 1 μ to 2.5 μ. The most prominent emission bands of the chemiluminescence spectrum Fig. 1, at 1.27 μ, 1.43 μ, and 1.51 μ, are also observed in absorption. Also, the 1.51 μ absorption band is shifted to 2.02 μ upon deuteration, while the other bands remain unchanged, in agreement with the emission spectrum.

Work is in progress to obtain higher resolution spectra of the chemiluminescence due to reaction (2). A more detailed analysis of the spectrum is necessary to establish the energy difference between the lowest vibrational levels of the ground and first excited states of HO_2. Also, the possibility of energy transfer from $O_2(^1\Delta_g)$ contributing to the excitation of HO_2 has to be further investigated.

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