

# Continuous Molecular Opacities and Photodissociation

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## 1 Introduction

It is well known that molecules have much more complex electronic spectra than atoms due to their rotational and vibrational motions. Most molecular spectra observed in the laboratory and included in model atmospheres involve transitions between two bound electronic states. However, in contrast to atoms, molecules can also have bound–free transitions into states that are repulsive in at least one nuclear coordinate, even below the first ionization potential. These transitions not only lead to dissociation of the molecule, but also provide a source of continuous opacity which is usually not taken into account in model atmospheres. Moreover, photodissociation plays an important role in the non-LTE chemistry of stellar atmospheres and circumstellar envelopes (see Olofsson this volume). In this chapter, a brief overview of our current knowledge of cross sections for continuous absorption and photodissociation is given.

## 2 Absorption Processes

The processes of bound–bound and bound–free absorption are illustrated in Fig. 1 for a diatomic molecule. In the first case, a discrete spectrum consisting of sharp lines occurs corresponding to transitions into the various vibration–rotation levels of the excited electronic state. In the second case, a broad continuous spectrum arises. The peak of this cross section occurs close to the vertical excitation energy and its width is determined by the steepness of the repulsive potential: the steeper the potential, the broader the cross section. The shape reflects that of the ground–state vibrational wave function; the case illustrated in Fig. 1 refers to a molecule initially in its lowest  $v'' = 0$  vibrational level. Cross sections for absorption out of higher vibrational levels  $v'' > 0$  would show a nodal structure.

Continuous absorption starts at energies just above the lowest dissociation energy of the molecule, but usually peaks at much higher energies. An extreme case is formed by the  $\text{H}_3^+$  ion: its dissociation energy is  $\sim 5$  eV, but its first continuous absorption channel only occurs around  $\sim 18$  eV. For simple hydrides such as

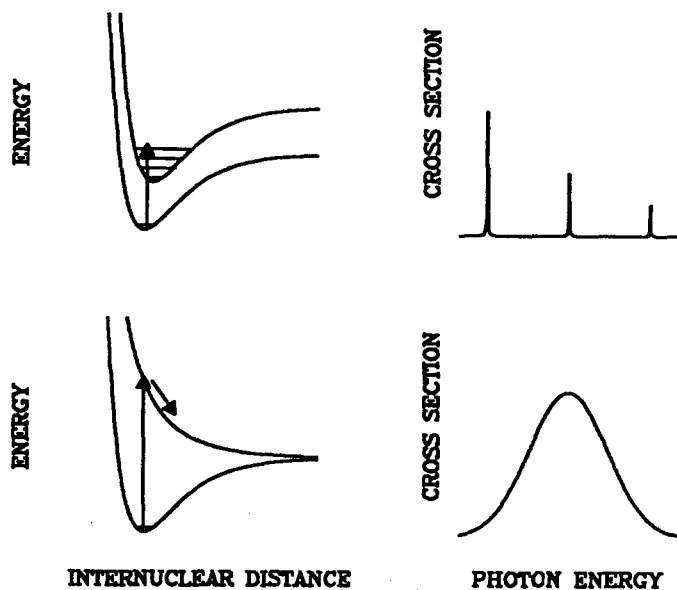


Fig. 1. Potential energy curves illustrating the processes of bound-bound and bound-free absorption for a diatomic molecule.

CH, OH, NH, CH<sub>2</sub> and H<sub>2</sub>O, the dissociation energy to ground-state products is typically 4–5 eV, so that continuous absorption can occur at  $\lambda < 3000 \text{ \AA}$ . For heavy diatomic and polyatomic molecules containing only first-row atoms (e.g. C<sub>2</sub>, CO, CN), the dissociation energy is usually much larger, ranging from 6.2 eV (C<sub>2</sub>) to 11.1 eV (CO). Continuous absorption for these molecules starts at wavelengths  $< 2000 \text{ \AA}$  (C<sub>2</sub>) to  $< 1100 \text{ \AA}$  (CO) and is much less important. For heavy molecules involving second row atoms such as SiC, however, the dissociation energy is only  $\sim 4 \text{ eV}$ , so that continuous absorption for these species is also likely to be significant.

### 3 Photodissociation Processes

Virtually all of the continuous absorptions shown in Fig. 1 lead to dissociation of the molecule, since spontaneous emission back to the electronic ground state is a comparatively slow process. This process of *direct photodissociation* is the most efficient way for molecular dissociation to occur, but indirect processes can play a significant role as well. These processes are summarized in Fig. 2, and are initiated by discrete absorptions into bound excited states. More detailed reviews of the photodissociation of astrophysical molecules have been given by van Dishoeck (1988) and Kirby & van Dishoeck (1988).

In the process of *predissociation*, the excited bound state interacts non-radiatively with a nearby repulsive electronic state, resulting in eventual dis-

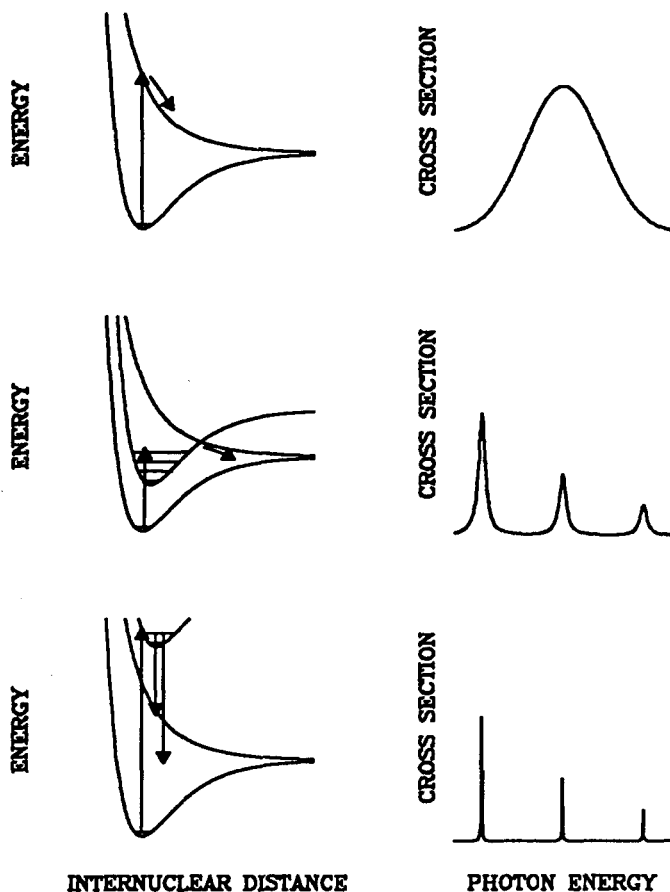


Fig. 2. Potential energy curves illustrating the processes of photodissociation for a diatomic molecule. Top: direct photodissociation; middle: predissociation; bottom: spontaneous radiative dissociation. The corresponding photodissociation cross sections as functions of energy are shown as well.

sociation of the molecule. The strength of the interaction depends on the type of coupling (e.g. spin-orbit) and on the energy level involved, but the corresponding predissociation rates are typically comparable to or larger than the rates for spontaneous emission. The effective photodissociation cross section consists in this case of a series of discrete peaks. The strength of each peak reflects the product of the oscillator strength of the initial absorption and the dissociation efficiency of the level involved. The width is controlled by the sum of the radiative and predissociation rates and is typically of order  $1 \text{ cm}^{-1}$  if the predissociation is rapid.

If the excited bound states are not predissociated, *spontaneous radiative dissociation* can still be effective through emission of photons into the continuum

of a lower-lying repulsive state or the vibrational continuum of the ground electronic state. The efficiency of the process is in this case determined by the competition with spontaneous emission into lower-lying bound states. The photodissociation cross section again consists of a series of discrete peaks, but the peaks are not broadened and have small widths ( $<0.01 \text{ cm}^{-1}$ ) determined by the total radiative lifetime.

Because a molecule has many excited electronic states, in general all of these processes will occur. However, usually only one of them dominates the photodissociation of a molecule under astronomical circumstances. For example, the photodissociation of simple hydrides like CH, CH<sup>+</sup>, NH, OH, H<sub>2</sub>O and CH<sub>2</sub> proceeds mostly through the direct process. On the other hand, the photodissociation of CO is controlled by predissociation processes, whereas that of H<sub>2</sub> occurs by spontaneous radiative dissociation. Whether the photodissociation is dominated by continuous or line processes has important consequences for the radiative transfer through, for example, a circumstellar shell, because in the latter case the lines can become optically thick if the abundance of the molecule is sufficiently high.

The photodissociation rate  $k_{pd}$  (in  $\text{s}^{-1}$ ) of a molecule by continuous absorption is given by

$$k_{pd}^{cont} = \int \sigma(\lambda) I(\lambda) d\lambda \text{ s}^{-1},$$

where  $\sigma$  is the cross section for photodissociation in  $\text{cm}^2$  and  $I$  is the mean intensity of the radiation in photons  $\text{cm}^{-2} \text{ s}^{-1} \text{ \AA}^{-1}$  as a function of wavelength  $\lambda$  in  $\text{\AA}$ . For the indirect processes of predissociation and spontaneous radiative dissociation, the rate of dissociation by absorption into a specific level of a bound upper state  $u$  from lower level  $\ell$  is

$$k_{pd}^{line} = \frac{\pi e^2}{mc^2} \lambda_{ul}^2 f_{ul} \eta_u x_\ell I(\lambda_{ul}) \text{ s}^{-1},$$

where  $f_{ul}$  is the oscillator strength,  $\eta_u$  is the dissociation efficiency of the upper level which lies between 0 and 1, and  $x_\ell$  is the fractional population in level  $\ell$ . The total rate is obtained by summing all the continuous and discrete processes.

In circumstellar envelopes, the radiation responsible for dissociating the molecules is provided mostly by the interstellar radiation field, which extends from the Lyman limit at extreme ultraviolet wavelengths (912  $\text{\AA}$ ) to infrared wavelengths. In the atmospheres of late-type stars, many fewer ultraviolet photons are found. A recent discussion of the interstellar radiation field has been given by van Dishoeck (1993). Reviews of interstellar photodissociation rates have been presented by van Dishoeck (1988) and Roberge et al. (1991).

## 4 Experimental Data

Laboratory measurements of absorption cross sections have been obtained over a broad wavelength range for most chemically stable species, including H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> (see Lee 1984 for a summary). Most of these experiments

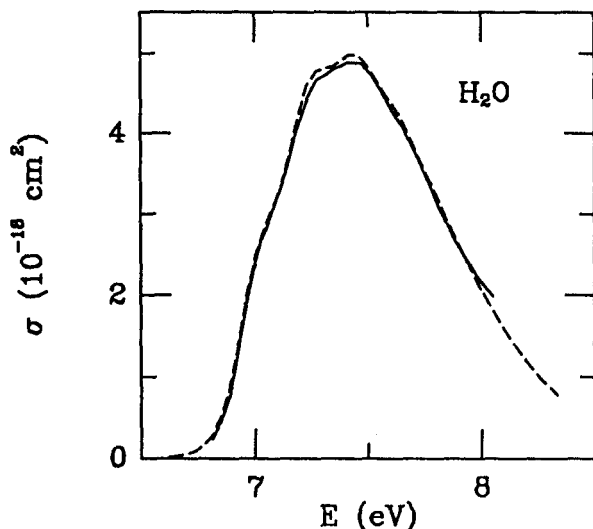
have been performed at rather low spectral resolution in which individual lines of transitions to bound excited states are not resolved. Although the continuous cross sections due to absorption into repulsive excited states are quite accurate in such measurements, the cross sections for discrete absorptions are very uncertain. Moreover, most experiments do not measure the fluorescence efficiency for such discrete transitions, so that it is often difficult to obtain information on the probability  $\eta_u$  for predissociation processes. Very high spectral resolution experiments at low pressures are essential to obtain reliable data for these discrete absorptions. Note that even for chemically stable molecules, little information is available on cross sections at extreme ultraviolet wavelengths below 1200 Å, CO being the major exception (see below). Although some beautiful experiments have been performed using far-ultraviolet lasers, these are usually limited to only a few specific wavelengths. Experimental data on the photodissociation of reactive molecules such as the radicals CH, OH, CH<sub>2</sub>, and C<sub>2</sub>H, are still virtually non-existent. Reviews on cross section measurements have been given e.g. by Hudson (1971), Okabe (1978), Ashfold et al. (1979), Lee (1984) and Huebner et al. (1992).

One important circumstellar molecule for which significant experimental progress has been made in the last 6 years is CO. CO is an enormously stable molecule with a dissociation energy of 11.09 eV corresponding to a threshold of 1118 Å. The detailed laboratory spectra of Letzelter et al. (1987) established that no continuous absorption occurs longward of 912 Å, but that the CO photodissociation is dominated by line absorptions in about 30 bands, most of which are strongly predissociated. Subsequent experiments by Stark et al. (1991, 1993), Eidelsberg & Rostas (1990), Eidelsberg et al. (1991), Smith et al. (1991), Levelt et al. (1992), Eikema et al. (1993) and Drabbels et al. (1993) have extended this work to other isotopes and much higher spectral resolution. Although some uncertainties still persist in the oscillator strengths and predissociation rates of individual lines (Kirby & Cooper 1989; Stark et al. 1992; Chan et al. 1993), these are not expected to change much the overall photodissociation rate. The depth dependence of the CO photodissociation rate in circumstellar envelopes is affected not only by self-shielding, but also by shielding by H and H<sub>2</sub> because they absorb in the same wavelength region. <sup>12</sup>CO, in turn, can shield the less abundant <sup>13</sup>CO and C<sup>18</sup>O species. Thus, a complete numerical simulation of the entire spectrum of <sup>12</sup>CO, <sup>13</sup>CO, C<sup>18</sup>O, H<sub>2</sub> and H is required to compute correctly the attenuation at each depth into the envelope (van Dishoeck & Black 1988; Viala et al. 1988; Mamon et al. 1988).

## 5 Theoretical Calculations

The procedure for obtaining absorption and photodissociation cross sections from theory has been outlined by Kirby & van Dishoeck (1988) for diatomic species and by Schinke (1993) for polyatomic molecules. The first step is to obtain potential energy curves or surfaces of the ground and excited electronic states using ab initio quantum chemical methods (see Langhoff & Bauschlicher

and Peyerimhoff, this volume). Such calculations can also provide the transition dipole moments connecting the excited states with the ground state. The second step is to solve the dynamical equations for the nuclear motions on these potential surfaces. This problem can be formulated either in a time-independent or a time-dependent manner. The former method is easy to apply to one-dimensional dissociation involving diatomic molecules, but becomes more cumbersome for multi-dimensional systems. Therefore, the time-dependent method is usually adopted to study the photodissociation of polyatomic molecules.



**Fig. 3.** Comparison between experimental and theoretical cross sections of  $\text{H}_2\text{O}$  in the  $\tilde{A}^1\text{B}_1 - \tilde{X}^1\text{A}_1$  absorption band. The experimental data (full line) are from van Hemert (1980, unpublished results); the theoretical results (dashed line) from Kroes (1992, unpublished results) (see also Engel et al. 1992).

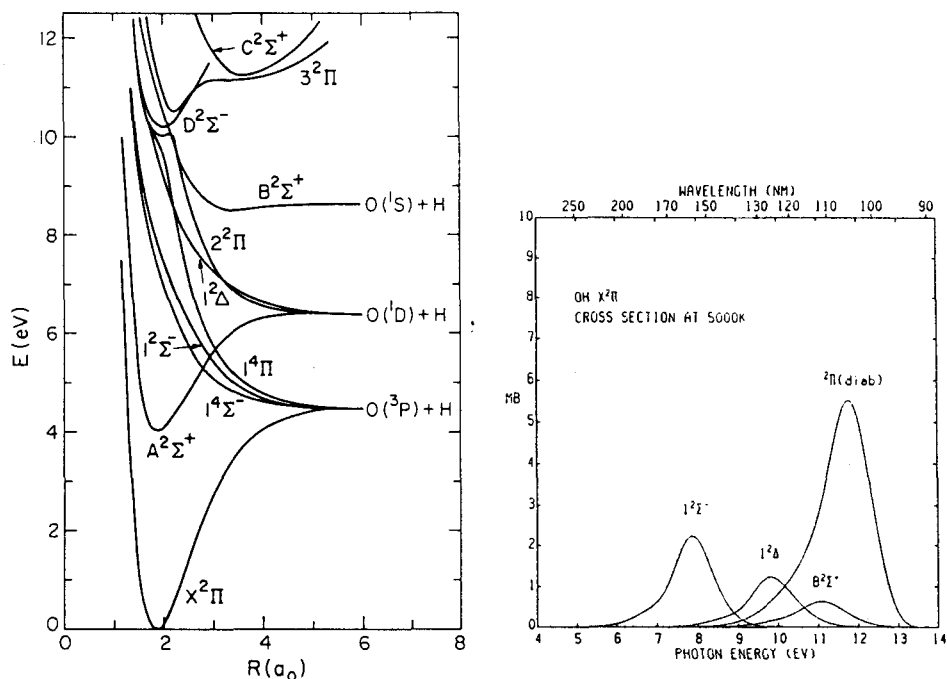
Theory can provide accurate results for small molecules (including radicals) in which the number of electrons is of order 30 or less. In practice, reliable results are limited to the lowest five electronic states per molecular symmetry. For such states, the uncertainty in the transition energies is typically 0.1–0.2 eV and the uncertainty in the transition dipole moments is 10% or less. The subsequent dynamics are in principle exact and are usually converged to better than 1%, although strong interactions between states can complicate the calculations. Overall, the cross sections have typical uncertainties less than 30% in absolute value and less than 0.2 eV in position.

As an example of the accuracy of the calculations, Fig. 3 shows a comparison between experiment and a fully 3-dimensional theoretical study of the absorption

of  $\text{H}_2\text{O}$  into its first excited electronic state. The theoretical cross sections were obtained using ab initio potential energy surfaces and a computed transition dipole moment, and contained no adjustable parameters except for a shift of  $-0.06$  eV in position. The agreement with experiment is remarkable, both in magnitude and shape of the cross section.

## 6 Examples

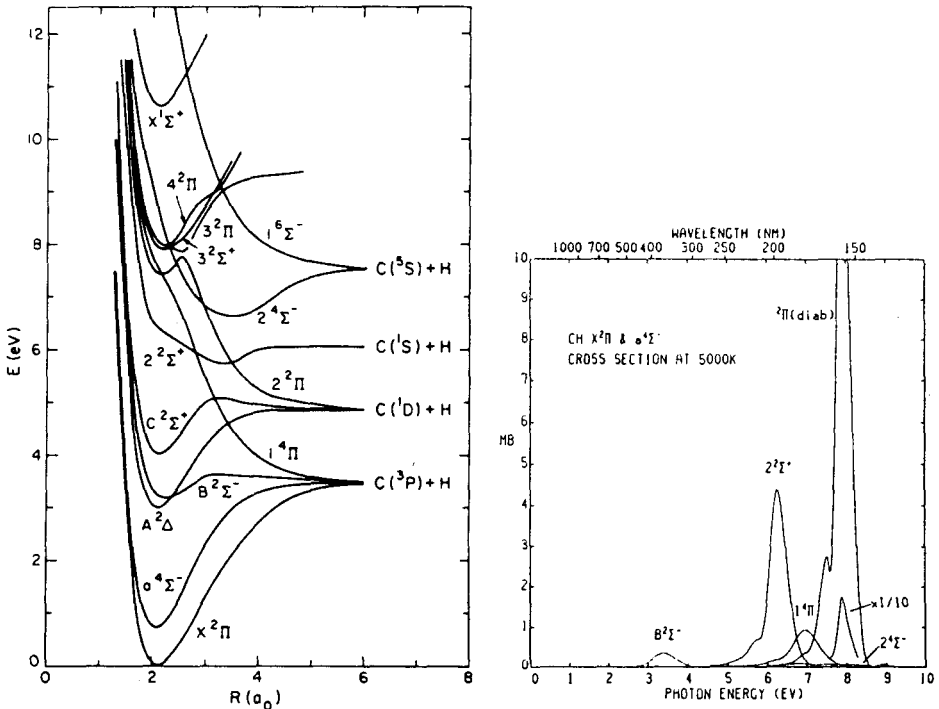
### 6.1 OH and CH



**Fig. 4.** Potential energy curves (left) and photodissociation cross sections at 5000 K (right) for the OH molecule (from: van Dishoeck & Dalgarno 1983; Kurucz et al. 1987).

The absorption and photodissociation processes of the OH radical have been studied in detail by van Dishoeck & Dalgarno (1983, 1984). In addition to the

well-known discrete absorption in the  $A^2\Sigma^+ - X^2\Pi$  transition at  $\sim 3000 \text{ \AA}$ , several continuous absorption channels have been found in the 1000–1900  $\text{\AA}$  range. The cross sections presented in Fig. 4 were obtained assuming that the population distribution over the lower vibrational levels is characterized by a temperature of 5000 K (Kurucz et al. 1987). Over the wavelength range 1000–3000  $\text{\AA}$ , the integrated cross section for discrete transitions,  $\int \sigma_{\text{line}}(\lambda)d\lambda \approx 1 \times 10^{-15} \text{ cm}^2 \text{ \AA}$ , is smaller than that for continuous absorption,  $\int \sigma_{\text{cont}}(\lambda)d\lambda \approx 2 \times 10^{-15} \text{ cm}^2 \text{ \AA}$ .

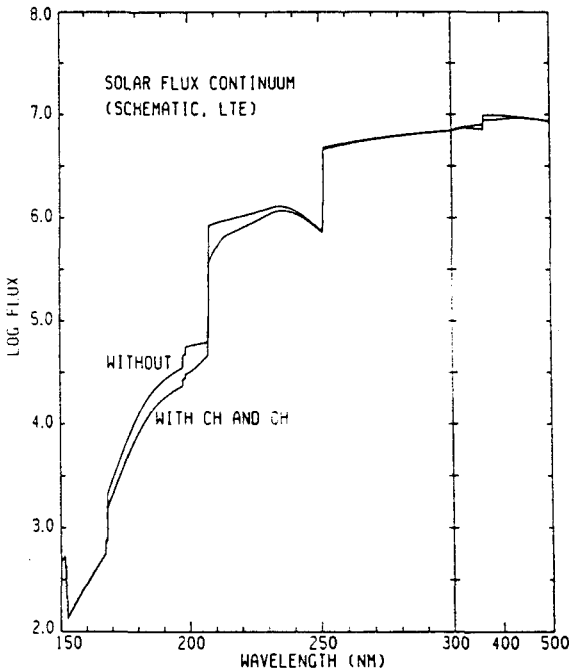


**Fig. 5.** Potential energy curves (left) and photodissociation cross sections at 5000 K (right) for the CH molecule (from: van Dishoeck 1987; Kurucz et al. 1987).

A similar study has been performed for CH by van Dishoeck (1987), which is illustrated in Fig. 5. In this case, the integrated absorption in discrete lines,  $\int \sigma_{\text{line}}(\lambda)d\lambda \approx 3.6 \times 10^{-15} \text{ cm}^2 \text{ \AA}$ , is comparable to the integrated continuous



absorption,  $\int \sigma_{\text{cont}}(\lambda)d\lambda \approx 3.5 \times 10^{-15} \text{ cm}^2 \text{ \AA}$ , over the wavelength range 1000–5000 Å.



**Fig. 6.** Solar ultraviolet continuum flux (in  $\text{erg cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1} \text{ nm}^{-1}$ ) computed with and without inclusion of OH and CH continuous absorption.

The effect of the CH and OH opacities on the solar continuum has been investigated by Kurucz et al. (1987) using Allen’s (1978) LTE solar model in Kurucz’s spectrum synthesis program (Kurucz & Avrett 1981) without including line absorptions. The result is presented in Fig. 6. Below 1500 Å, the continuum of the Sun is formed mostly in the chromosphere where the contribution of OH and CH is negligible. However, between 1700 and 2500 Å, OH and CH affect the continuum ultraviolet flux by tens of percent. When line opacity is included in the models, the relative effect will be smaller, but it remains relatively important in regions between the lines.

### 6.2 NH and CH<sub>2</sub>

The potential energy curves and cross sections for the NH molecule have been computed by Kirby & Goldfield (1991). As for OH and CH, several continuous dissociation channels are found, although they start at quite high energies,  $\lambda < 1700 \text{ \AA}$ .

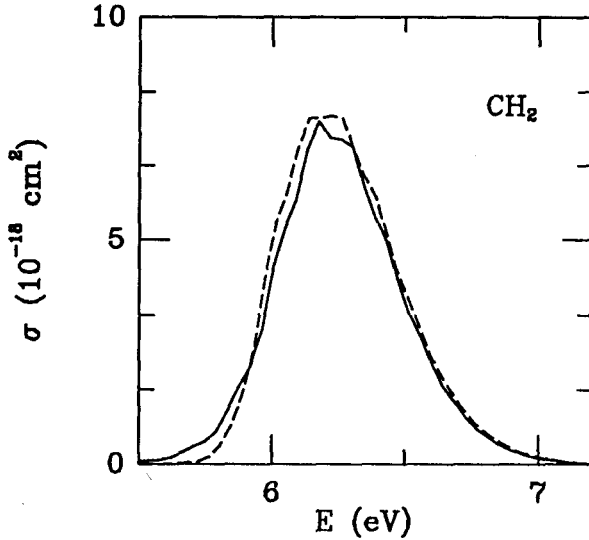


Fig. 7. Photodissociation cross sections for absorption into the first excited triplet state of  $\text{CH}_2$  obtained with a fully 3-dimensional dynamical calculation (full line) and with a 2-dimensional calculation keeping the angle fixed at  $\alpha_{\text{eq}}=134^\circ$  (dashed line) (from: Kroes et al. 1993).

The photodissociation processes of the  $\text{CH}_2$  molecule have recently been investigated in a series of papers by Beärda et al. (1992) and Kroes et al. (1993). Fully 3-dimensional potential energy surfaces and transition dipole moment functions have been obtained for the lowest ten states of triplet symmetry of the molecule. The subsequent dynamics for dissociation in the first absorption band have been solved in 2- and 3-dimensions, with good agreement between the two cases. If this result would apply more generally, substantial computational savings could be obtained. The cross sections are presented in Fig. 7.

## 7 Conclusions

It has been shown that continuous molecular opacity due to bound-free absorptions above the dissociation energy may have a non-negligible effect on stellar atmosphere continua. For many simple molecules of astrophysical relevance, the integrated cross sections for continuous absorption are comparable to those for discrete absorptions. The continuous absorptions also lead to photodissociation of the molecules, a process which plays an important role in the non-LTE chemistry in stellar atmospheres and circumstellar envelopes.

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