Gas-phase UV cross sections of radicals

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Abstract. We present some new studies of the absolute photodissociation cross sections of astrophysically-relevant diatomic radicals.

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1. Introduction

A century of classical electronic spectroscopy has provided quantitative photoprocess cross sections spanning an enormous number of species and wavelength ranges. But challenges remain in the far-, vacuum-, and extreme-ultraviolet wavelengths where radical species are concerned. This is due to the difficulty of obtaining measurable column densities and the complexity of predicting overlapping high-energy states. Another difficulty with studying open-shell molecules is that fine structure of both ground and excited states leads to a complicated overlap of rotational lines. This problem is worsened where the excited state is heavily predissociated and lifetime broadening leads to further line confusion.

Nonetheless, the quantitative interpretation of ongoing remote and in-place observations of ultraviolet-irradiated planetary atmospheres and interstellar gas relies on accurate photoabsorption and photodissociation cross sections, not all of which are known. One case where fine isotope-dependent details count is in geochemical or remote observations of isotope fractionation where this can be traced to a photolytic origin.

Below is a summary of four studies we have made of atmospherically- or astrophysically-relevant radical cross sections to address data needs in the astrochemical and photochemical communities.

2. Results

2.1. OH $D \leftarrow X$

This molecule is widely observed in the interstellar medium and cometary comae where it is itself a photolysis product of water. Its photodissociation cross sections is well-studied theoretically (van Dishoeck & Dalgarno (1984)) but not measured experimentally. Using the far-ultraviolet-capable Fourier-transform spectrometer and bright synchrotron
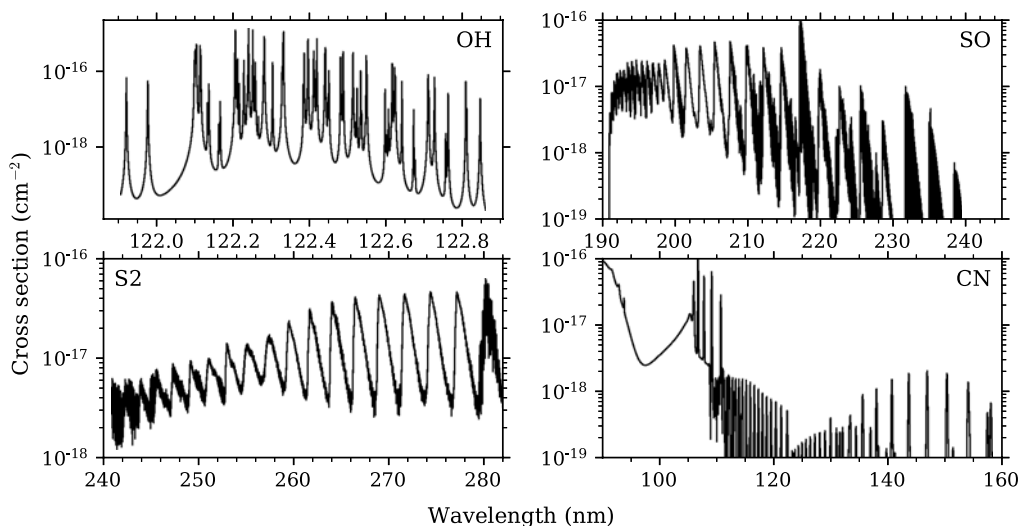
Figure 1. The new photodissociation cross sections. *OH*: Effective Hamiltonian model of the $D(0) \leftarrow X(0)$ band. *SO*: Global model of interacting $B(v_B) \leftarrow X(0)$ and $C(v_C) \leftarrow X(0)$ bands. S_2: Experimental cross section at 370 K. *CN*: Ab initio electronic-vibrational spectrum.

radiation source at the DESIRS beamline of the SOLEIL synchrotron (de Oliveira *et al.* (2016)) we recorded two photoabsorption bands of the $D\,^2\Sigma^+ \leftarrow X\,^2\Pi$ system (Heays *et al.* (2018)).

2.2. *CN highly-excited states*

CN is another astrophysically prevalent molecule in irradiated environments where its lifetime is limited by photodissociation of its highly-excited unbound states. We performed a new quantum-chemical calculation of these states and their absorption properties employing a CASSCF calculation with as large an active-space as feasible followed by multi-reference configuration interaction computation. The challenge of this calculation arises due to the high density of vacuum-ultraviolet accessible doublet-states approaching the 91.2 nm Lyman-limit, due to the relatively low ionisation threshold of CN. A further computation found spin-orbit predissociation of low-lying bound excited states through a nonradiative intersystem transition into unbound quartet states. This leads to a weak photodissociation cross section in the far-ultraviolet which is nonetheless significant in long-wavelength dominated radiation fields.

2.3. S_2 $B \leftarrow X$

Photoabsorption by the $B(v) \leftarrow X(0)$ bands dominates dissociation of S_2. This radical was generated as sulphur vapour in an oven at around 800 K and in a microwave discharge nearer room temperature (Stark *et al.* (2018)). Fourier-transform absorption spectroscopy was use to measure cross sections between 240 and 285 nm. This data was used to constrain a coupled-channels model of the $B\,^3\Sigma_u^-$ state and its predissociation (Lewis *et al.* (2018)). This predissociation is evident in the experimental cross section shown in Fig. 1 where only the longest-wavelength electronic-vibrational band shows clear rotational structure.

2.4. *SO B ← X and C ← X*

Fourier-transform spectra of SO generated in a microwave discharge through SO_2 was recorded for four isotopologues. An experimental difficulty in this case arose from heavy contamination by parent SO_2. Isotope-independent potential-energy curves and a $B\,^3\Sigma^- \sim C\,^3\Pi$ spin-orbit interaction was deduced from this experimental data. A 380 K photodissociation cross section for $^{32}S^{16}O$ computed by this model is shown in Fig. 1.

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