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Absorption cross section of molecular oxygen in the transition $E\ {}^3\Sigma_u^-\ v = 0 - X\ {}^3\Sigma_g^-\ v = 0$ at 38 K

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ABSTRACT

Aims. This investigation was undertaken to determine the absorption cross sections of oxygen in the VUV region at temperatures <50 K.

Methods. The absorption spectra of gaseous samples cooled with a slit jet and near 300 K were measured with the same absorption system coupled to the VUV beam line of a synchrotron.

Results. The maximum absorption cross section for the transition from $X\ {}^3\Sigma_g^-\ v = 0$ to state $E\ {}^3\Sigma_u^-\ v = 0$ for ${}^{16}O_2$ at 38 K was determined to be 98.7 Mb (or 9.87×10^{-18} cm^2). The value of this maximum absorption cross section at 38 K is 1.7 times the value at 303.7 K.

Key words. astronomical databases: miscellaneous – molecular data – techniques: spectroscopic – ultraviolet: general

1. Introduction

To assess photochemically induced changes in stellar media, one must have quantitative information about the absorption cross sections of pertinent molecular species in the vacuum-ultraviolet (VUV) range (Miller & Yung 2000). We determined the absorption cross sections of several interstellar molecular species in this range (H_2O, Cheng et al. 1999, 2004; HCl, Bahou et al. 2001; CH_4, Lee et al. 2001; CH_3OH, Cheng et al. 2002; NH_3, Cheng et al. 2006; and Liang et al. 2007), but most measurements were made near 300 K. One problem in the application of these data to the photochemical model is that in outer space the temperature is much less than 300 K: for example, the relevant atmospheric temperature is ~170 K for Jupiter, ~140 K for Saturn, ~120 K for Titan, ~50 K for Triton, and even lower for Neptune and Uranus (Yung & DeMore 1999). Molecular absorption cross sections measured near 300 K are generally inadequate to explain the observed spectral features and to allow an accurate determination of the abundance of atmospheric constituents in outer space. It is thus preferable to measure directly the absorption cross sections at temperatures <50 K. Another problem is that thermal motion and the population of energetic states blur many pertinent features of VUV spectra of samples near 300 K. If we can obtain spectra of these species <50 K, we can provide information to define an accurate potential-energy surface for theoretical consideration and the dissociation dynamics of interstellar molecules.

To measure the absorption spectra in the VUV region of planetary molecules at temperatures <50 K, we constructed a slit-jet absorption system that is connected to a VUV beamline of a synchrotron at National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Using this setup we have measured the absorption spectra of several molecules of interest; we discuss here the results for O_2.

Oxygen not only is a highly important gas on Earth but also has been detected in cold, outer planetary systems and in deep space. Although VUV absorption cross sections of O_2 have been extensively investigated (Gibson et al. 1983; Hudson et al. 1966; Huffman 1969; Kanik et al. 1997; Metzger & Cook 1964; Ogawa 1975; Wang et al. 1987; Yoshino et al. 2005, and references therein), the least temperature of a recording was 79 K, which is still not low enough for an understanding of the astrophysical spectral properties of O_2. For this reason accurate measurement of data of O_2 for temperatures below 79 K is important.

2. Experiments

We measured the absorption spectra of gaseous samples cooled with a slit jet and near 300 K at the same end station coupled to the VUV beam line of a synchrotron, for which a systematic layout is displayed in Fig. 1. In brief, the gaseous stream from the jet intersected, in the absorption chamber, the beam of VUV radiation from a beam line of the synchrotron; the VUV light was dispersed with a high-flux cylindrical-grating monochromator (focal length 6 m). The intensity of VUV light was monitored through light reflected from a LiF beamsplitter placed before the absorption chamber and at 45° from the beam line. A small fraction of the reflected light passed one additional LiF plate and impinged on a glass window coated with sodium salicylate. The luminescent signal subsequently detected with a photomultiplier tube (Hamamatsu R943-02) in a photon-counting mode was employed for normalization.

The light transmitted through the LiF beam splitter crossed the cooled gaseous stream expanded from the slit jet (12.5 × 0.1 mm) in its absorption chamber, which was sealed with two LiF windows; the distance between these two windows was 0.050 m. The light transmitted through that absorption chamber

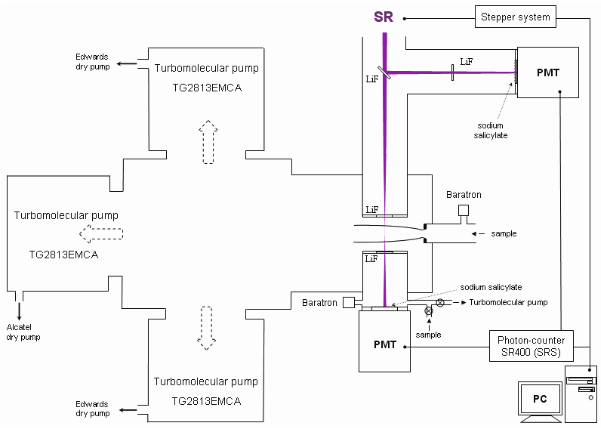

Fig. 1. Schematic diagram of the experiment.

irradiated a glass window coated with sodium salicylate. In the same way, the fluorescence was detected with a photomultiplier in a photon-counting mode. That absorption chamber was connected to three turbomolecular pumps (TG 2813 EMCA-03, Osaka Vacuum Ltd.) each having a pumping speed 2.8 $m^3 s^{-1}$. One pump was connected to a dry pump (Alcatel ADS 501, pumping speed 510 m^3/h) and the other two were connected to a dry pumping system (Edwards iQMB1200, pumping speed 940 m^3/h). Before measuring the absorption spectrum of a supersonically expanded sample, we evacuated the cell to 1 mPa with the turbomolecular pumping system.

The absorption spectrum of a gaseous sample near 300 K was also measured with this end station. The tube between the LiF exit window of the slit-jet absorption chamber and the phosphor-coated glass window served as a gaseous absorption cell near 300 K. While we recorded the absorption spectra of gaseous samples near 300 K, we charged this tube cell with a gaseous sample and stopped the flow of the jet. The density of gas in the cell was determined from the gaseous pressure monitored with a capacitance manometer (MKS-Baratron); the temperature was measured with a thermocouple. The absorption cross section, σ, is determined from the absorbance A according to $A = \ln(I_0/I) = n\sigma l + \alpha$, in which I_0 and I are incident and transmitted light intensities, respectively; n is the number density of the gas, and l (=8.47 cm) is the length of the path of gaseous absorption. The offset, α, was determined at $n = 0$, when the gas cell was pumped below 1 mPa. At each wavelength, a value of σ was obtained from a linear fit of 4–6 absorbances measured at varied gaseous pressures.

Oxygen (purity 99.999%, Matheson) was used without further purification. The wavelength was calibrated with absorption lines of Xe (Yoshino & Freeman 2005), CO (Tilford et al. 1965; Simmons et al. 1969) and H_2O (Wang et al. 1977); the accuracy of a measured wavelength is limited by the scan step.

3. Results and discussion

With the VUV absorption system we measured samples of the same gas in two modes – for the static gas near 300 K and for the gas flowing through the slit jet. Absolute cross sections for the absorption of O_2 at 303.7 K appear in Fig. 2A for spectral regions 115–180 nm. Considering all possible systematic errors, we estimate experimental uncertainties of cross sections to be within 10 per cent of our reported values. The absorption of O_2 in the spectral range 130–175 nm belongs to the Schumann-Runge continuum, for which we measured the cross sections at intervals 0.05 nm. Comparison of these cross sections with those of previous measurements near 300 K indicates that our data agree satisfactorily within the experimental uncertainty. For instance, Yoshino et al. (2005) reported the cross section at 143.26 nm and 295 K to be 14.2 Mb (1 Mb = 10^{-18} cm^2); our value is 15.4 Mb, 8 per cent larger than theirs. In the same region, Ogawa & Ogawa (1975) specified the cross section at 143.0 nm and 298 K to be 15.3 Mb, similar to our value 15.1 Mb. In other regions, we recorded the data at interval 0.02 nm; the maximum values are 57.6 Mb for state E $^3\Sigma_u^-$ at 124.44 nm, and 18.4 Mb for state a $^1\Delta_g$ at 120.54 nm . That these values agree satisfactorily with 57.6 and 16.2 Mb, reported by Ogawa & Ogawa (1975), demonstrates that our experimental system operates effectively.

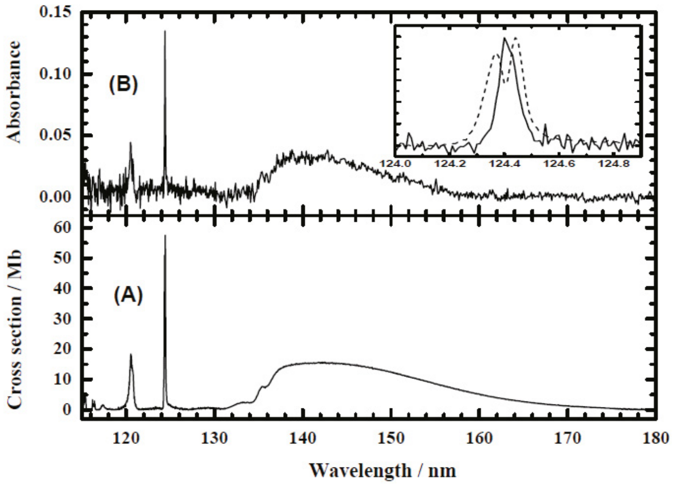

Fig. 2. Absorption spectra of O_2 in the wavelength range 115–180 nm: **A)** absorption cross section at 303.7 K; **B)** absorption spectrum of O_2 through the slit jet at stagnation pressure 26.7 kPa. Inset: expanded absorption spectra about 124.4 nm recorded with resolution 0.01 nm at 303.7 K (dashed line) and with the jet (solid line).

For the gas flowing through the slit jet, the corresponding absorption spectrum of oxygen recorded in spectral range 115–180 nm at stagnation pressure 26.7 kPa is displayed in Fig. 2B. Although at first glance the shape of the spectrum for the jet-expanded carrier resembles that for 300 K, scrutiny reveals significant differences. The inset in Fig. 2 compares the absorption into state E $^3\Sigma_u^-$ $v = 0$ in wavelength range 124–125 nm for the static gas at temperature 303.7 K and for the jet-expanded gas; the profiles of the absorption depend strongly on temperature. For absorption near 300 K, although the overlapping lines are not entirely resolved, two branches are discernible with branch P more intense than branch R; the half width of the resultant band is about 0.15 nm. For the carrier gas subjected to jet expansion, we observed only one main feature with half width 0.07 nm.

Using published parameters for widths of lines (Lewis et al. 1988) and for wavenumbers of states X $^3\Sigma_g^-$ $v = 0$ and E $^3\Sigma_u^-$ $v = 0$ of $^{16}O_2$ (Welch & Mizushima 1972), we simulated the absorption attributed to the transition E $^3\Sigma_u^-$ $v = 0 - X$ $^3\Sigma_g^-$ $v = 0$, using a Fano line shape (Lewis et al. 1988) for each individual contributing line in a region 80 200–80 500 cm^{-1} as a function of temperature. Although more accurate expressions for the rotational terms of states X and E are available (Steinbach & Gordy 1973), so as to ensure an accurate and consistent simulation we employed directly the expressions reportedly used to evaluate the specified parameters (Ogawa & Ogawa 1975). Our derived spectra reproduce faithfully both the reported spectra (Lewis et al. 1988) at 79 K and 295 K and our own spectrum

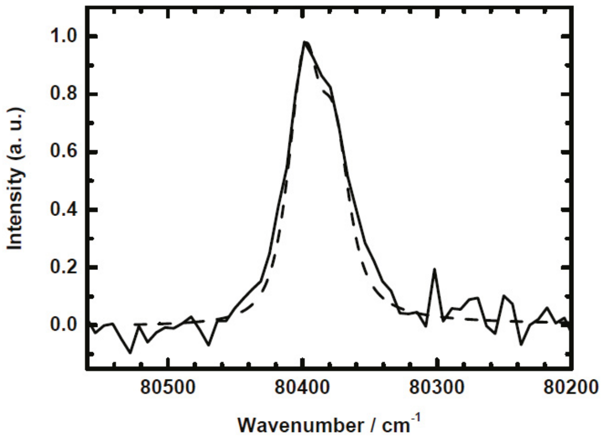

Fig. 3. Comparison of absorption spectra about 124.4 nm for jet-expanded O_2 (solid line) and simulation at 38 K (dashed line).

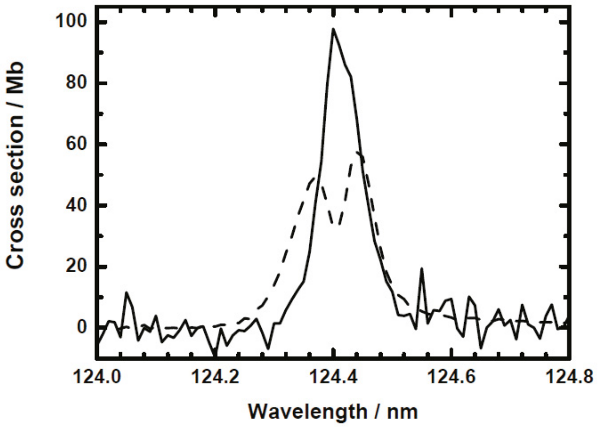

Fig. 4. Absorption cross sections about 124.4 nm of O_2 at 38 K (solid line) and 303.7 K (dashed line).

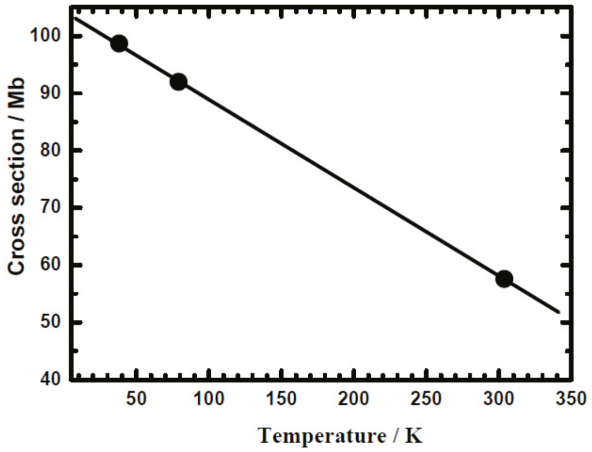

Fig. 5. Cross section at the wavelength of maximum absorption in the transition from state X $^3\Sigma_g^-$ $v = 0$ to state E $^3\Sigma_u^-$ $v = 0$ of $^{16}O_2$ vs. temperature.

of gaseous O_2 at 303.7 K. To derive the temperature of the jet-expanded gas, we then simulated the absorption spectra of O_2 from 15 K to 50 K and compared them with the experimental spectrum. By this means, we conclude that the temperature of the jet-expanded beam of O_2 at stagnation pressure 26.7 kPa is 38 ± 3 K; the absorption spectrum about 124 nm as simulated at 38 K and convoluted with resolution 7 cm^{-1} and as measured experimentally appear in Fig. 3. In the corresponding simulated spectrum of O_2 in thermal equilibrium at 38 K, the total absorption contains all six branches – three P branches and three R branches, but the R branches contribute most intensity; P and R branches are thus congested in a band with full width 45 cm^{-1} (0.07 nm) at half maximum.

As these absorption spectra have discrete structure, the measured absorption cross sections depend on the spectral slit width of the monochromator: the greater is the resolution, the larger is the apparent cross section at a maximum of absorption. For this reason, a comparison of absorption cross sections from separate authors is difficult, but integration of absorption cross sections over a spectral range yields an oscillator strength (f value) that is formally independent of monochromator slit width and is thus comparable for various experiments. The f value is calculated according to $f = 1.13 \times 10^{-6} \int \sigma \mathrm{d}\nu$, with absorption coefficient σ/ Mb and wavenumber ν/ cm^{-1}. Our f value for the transition E $^3\Sigma_u^-$ $v = 0$ – X $^3\Sigma_g^-$ $v = 0$ of O_2 in the spectral range 124–125 nm at 303.7 K is 0.00665, which is near the value 0.00625 reported by (Lewis et al. 1988). Because, in our work, the absorption spectra of O_2 near 300 K and for jet-expanded conditions were measured with the same optical parameters, it is possible to derive the absorption cross section at the temperature of the jet-expanded sample based on the oscillator strength obtained at 303.7 K. With this scheme and a value $f = 0.00665$, the absorption cross section of O_2 at 38 K in transition E $^3\Sigma_u^-$ $v = 0$ – X $^3\Sigma_g^-$ $v = 0$ and spectral range 124–125 nm is derivable, as shown in Fig. 4. The maximum absorption cross section for the transition E $^3\Sigma_u^-$ $v = 0$ – X $^3\Sigma_g^-$ $v = 0$ of O_2 at 124.4 nm is thus calculated to be 97.8 Mb at 38 K, which is about 1.7 times the value for 303.7 K.

VUV spectra provide a powerful analytical tool that has been applied during spacecraft missions. For example, the Cassini Ultraviolet Imaging Spectrograph (UVIS) included channels for extreme ultraviolet (EUV) and far ultraviolet (FUV) spectral imaging to record VUV spectra for targets in outer space at very low temperatures (Ajello 2005; Esposito et al. 2005; Shemansky et al. 2005). To verify the spectra obtained with these spacecraft and to explain the photochemical model within the atmospheres of these cold targets, we require extensive optical data applicable at those temperatures. Our present values of the absorption cross section of O_2 at 38 K are applicable for this purpose and are thus valuable for astrophysical applications. In our work we obtained the maximum cross sections of O_2 for state E $^3\Sigma_u^-$ as 97.8 Mb at 38 K and 57.6 Mb at 303.7 K. Lewis et al. obtained 92 Mb at 79 K. These three cross sections exhibit a linear relation with temperature, as displayed in Fig. 5; by this means one can estimate a rough value for other temperatures.

4. Conclusion

In the spectral range 115–180 nm with a synchrotron as a source of VUV radiation, we measured absorption cross sections of O_2 in a stagnant sample at 303.7 K and in a flowing gas subjected to adiabatic expansion. Using published optical parameters, we simulated the absorption spectra for the transition E $^3\Sigma_u^-$ $v = 0$–X $^3\Sigma_g^-$ $v = 0$ in wavelength range 124–125 nm and concluded that the temperature of the expanded beam is 38 ± 3 K. Based on oscillator strength 0.00665 obtained for 303.7 K, the maximum absorption cross section of O_2 at 38 K for the transition into state E $^3\Sigma_u^-$ is derived to be 98.7 Mb, which is 1.7 times that for 303.7 K.

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