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# DETERMINATION OF SPECTROSCOPIC PROPERTIES OF ATMOSPHERIC MOLECULES FROM HIGH RESOLUTION VACUUM ULTRAVIOLET CROSS SECTION AND WAVELENGTH MEASUREMENTS

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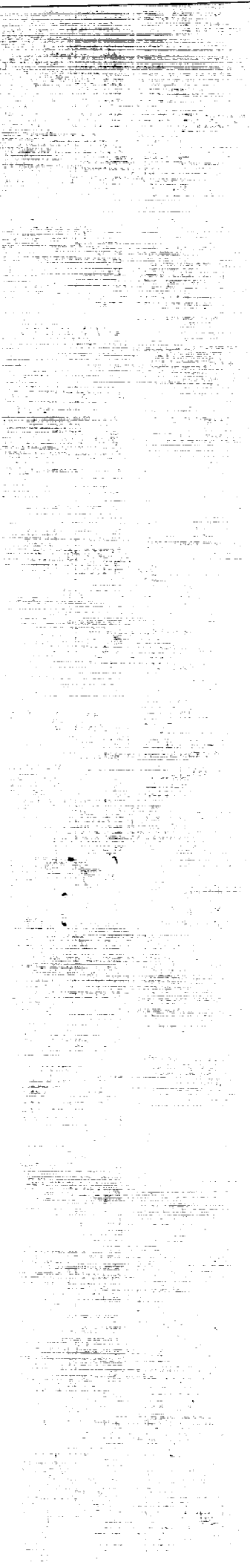

# 1 Abstract

An account is given of progress during the period 8/1/96-7/31/97 on work on (a) cross section measurements of $O_2$ S-R using a Fourier transform spectrometer (FTS) at the Photon Factory in Japan; (b) the determination of the predissociation linewidths of the Schumann-Runge bands (S-R) of $O_2$; (c) cross section measurements of $O_2$ Herzberg bands using a Fourier transform spectrometer (FTS) at Imperial College. and (d) cross section measurements of $H_2O$ in the wavelength region 120-188 nm. The experimental investigations are effected at high resolution with a 6.65 m scanning spectrometer and with the Fourier transform spectrometer. Below 175 nm, synchrotron radiation is most suitable for cross section measurements in combination with spectrometers at the Photon Factory, Japan. Cross section measurements of the Doppler limited bands depend on using the very high resolution, available with the Fourier transform spectrometer, (0.025 $cm^{-1}$ resolution). All of these spectroscopic measurements are needed for accurate calculations of the production of atomic oxygen, the penetration of solar radiation into the Earth's atmosphere, and photochemistry of minor molecules.

# 2 Progress Report for the Period 8/1/96-7/31/97

## 2.1 Cross section measurements of $O_2$ Schumann-Runge bands, $v' \geq 12$

We moved the FT spectrometer from Imperial College, London, UK to the Photon Factory, Japan under the co-operation and support of the United Kingdom, Japan and United States [Yoshino *et al.*, 1995a, 1996a]. K. Yoshino of CfA, A. P. Thorne and J. H. Murray of Imperial College, K. Ito and T. Matsui of Photon Factory, and T. Imajo of Kyushu University have been closely involved with VUV FT spectrometer work at the Photon Factory.

The radiation from the synchrotron is passed through the predisperser and the output is a strong continuum with the limited bandwidths of 20 to 40 Å. We examined the effects of resolution on the spectrum of the $O_2$ bands. The band head area of the (14,0) band is shown in Fig. 1, where the effects of different resolution, 0.06, 0.12, 0.20, and 0.30 $cm^{-1}$, are clearly demonstrated. We obtained 23 data files on the S-R measurements covering the wavelength region 175-185 nm with resolution of 0.06 and 0.12 $cm^{-1}$as shown in Table. 1. The $O_2$ column densities were varied from $1.53 \times 10^{17}$ to $25.6 \times 10^{17}$ $cm^{-2}$. The $S/N$ ratio was 30 to 100, depending on resolution and the number of co-added interferograms.

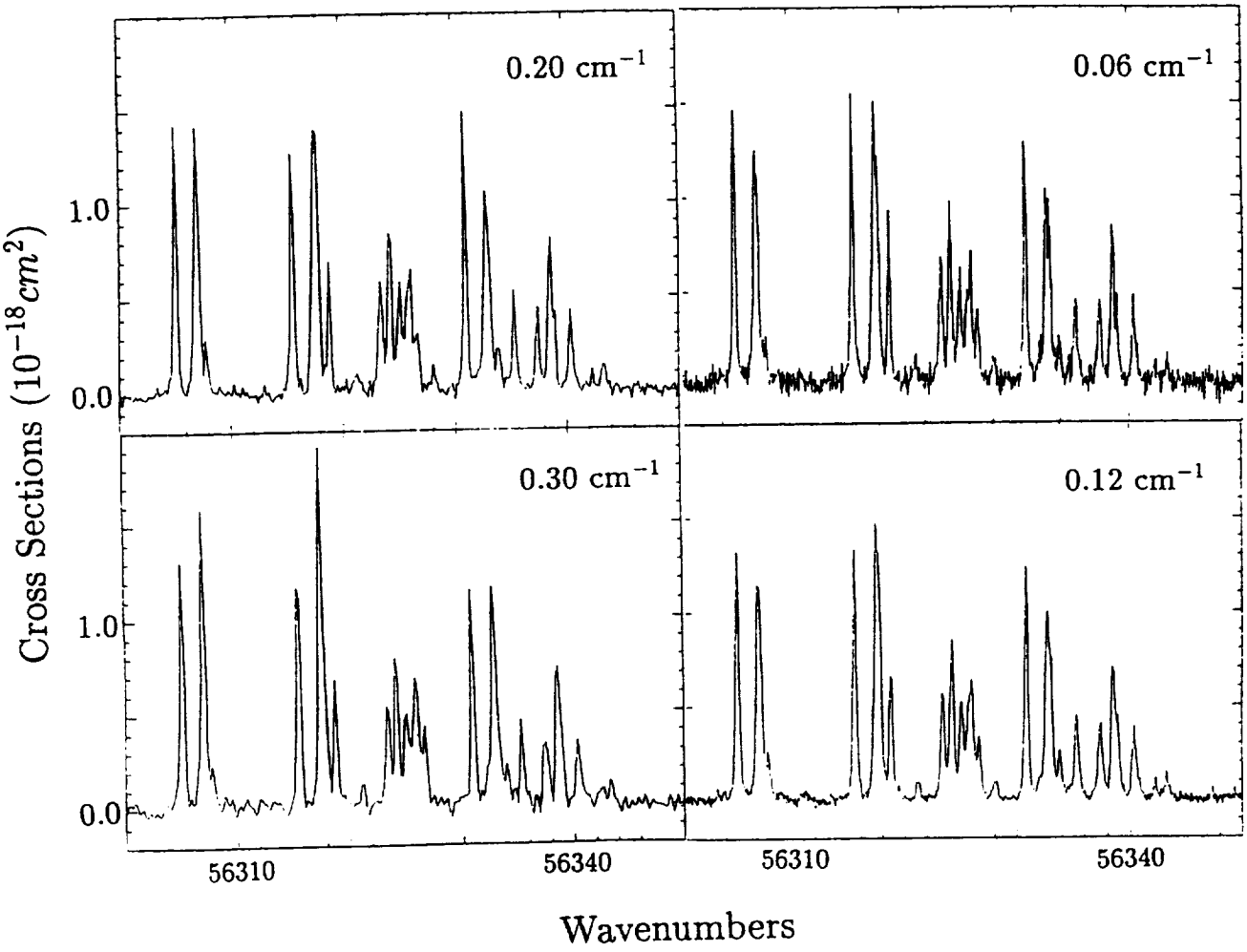


Figure 1: The cross sections of the (14,0) band of the Schumann-Runge system of $O_2$ with four values of resolution

Table 1 Measurements of the Schumann-Runge bands of $O_2$

| WL Å | Widths Å | Res. $cm^{-1}$ | Temp. K | $l$ cm | Pressure Torr | File | Co-Add | $S/N$ |
|---|---|---|---|---|---|---|---|---|
| 1790 | 40 | 0.06 | 295 | 7.82 | 4.0 | su319r | 46 | 29 |
| 1800 | 25 | 0.06 | 295 | 7.82 | 4.0 | tu321r | 66 | 43 |
| 1775 | 25 | 0.06 | 295 | 7.82 | 3.95 | we322r | 80 | 41 |
| 1775 | 25 | 0.06 | 78 | 7.82 | 1.00 | thu323r | 43 | 16 |
| 1850 | 25 | 0.06 | 295 | 7.82 | 8.75 | fr324r | 64 | 33 |
| 1825 | 25 | 0.06 | 295 | 7.82 | 4.08 | sa325r | 115 | 48 |
| 1820 | 25 | 0.06 | 295 | 7.82 | 1.00 | su326r | 95 | 37 |
| 1775 | 25 | 0.06 | 295 | 7.82 | 8.00 | tu328r | 118 | 39 |
| 1775 | 25 | 0.06 | 295 | 7.82 | 1.00 | we329r | 108 | 36 |
| 1775 | 25 | 0.06 | 295 | 7.82 | 2.00 | fs401r | 216 | 54 |
| 1775 | 25 | 0.06 | 295 | 7.82 | 2.00 | ts402r | 198 | 53 |
| 1850 | 25 | 0.06 | 295 | 7.82 | 4.00 | we405r | 128 | 55 |
| 1775 | 25 | 0.06 | 78 | 7.82 | 0.60 | tf407r | 102 | 32 |
| 1800 | 25 | 0.30 | 295 | 7.82 | 4.00 | sa03r | 32 | |
| | | 0.20 | 295 | 7.82 | 4.00 | sa02r | 64 | 60 |
| | | 0.10 | 295 | 7.82 | 4.00 | sa01r | 112 | 55 |
| 1850 | 25 | 0.12 | 295 | 7.82 | 8.70 | su409ar | 96 | 65 |
| 1850 | 25 | 0.12 | 295 | 7.82 | 4.00 | su409br | 96 | 63 |
| 1800 | 25 | 0.12 | 295 | 7.82 | 4.00 | tw412r | 451 | 103 |
| 1800 | 25 | 0.12 | 295 | 7.82 | 2.00 | tf413r | 400 | 95 |
| 1775 | 25 | 0.12 | 295 | 7.82 | 4.00 | sa415r | 496 | 103 |
| 1775 | 25 | 0.12 | 295 | 7.82 | 2.00 | su416r | 208 | 69 |
| 1770 | 20 | 0.12 | 295 | 7.82 | 10.0 | tu418r | 229 | 99 |

The absorption cross sections were fitted to Voigt profiles using the spectral reduction routine called GRELIM. Line parameters are determined through a non-linear least-squares procedure that iterates between the observed cross section and a synthetic spectrum corresponding to the experimental conditions. An absorption line profile of the Schumann-Runge bands is the convolution of the Lorentzian profile from predissociation and the Gaussian profile from Doppler broadening and the instrumental function. The broadening of a rotational line due to thermal molecular motion (Doppler), and the instrument (slit function) are close to Gaussian. These contributions to the total Voigt profile are respectively 0.12 $cm^{-1}$ and 0.15 $cm^{-1}$ for the spectra recorded with resolution of 0.06 $cm^{-1}$ and 0.12 $cm^{-1}$.

After the complete analysis of predissociation linewidth measurements of the Schumann-Runge bands, we realized that the Gaussian component, Doppler plus instrumental

widths, should not be presented as 0.12 and 0.15 $cm^{-1}$. We noticed a slight shift in spectral positions in individual data files due to a slight angular shift of the radiation from the synchrotron beam. The co-adding of these files resulted in broadened line shapes. We examined the $\gamma(3,0)$ band of NO at 196 nm, where the absorption line shape is purely Gaussian, and the observed a total linewidth as 0.170 to 0.190 $cm^{-1}$. These values lead to an instrumental width of 0.12 to 0.15 $cm^{-1}$. We also have recorded an absorption line of mercury at 189 nm, which consists of many isotopic lines. From these partially resolved isotopic lines, we estimated the instrumental widths of 0.125 $cm^{-1}$ which is in good agreement with NO measurements.

We will make the re-analysis of the Schumann-Runge bands, including line center positions, predissociation linewidths, and line and band oscillator strengths with the larger Gaussian widths.

## 2.2 Cross section measurements of Herzberg band II and III of $O_2$

Photoabsorption cross section measurements of the Herzberg bands (I through III) of $O_2$ have been made by Fourier transform spectrometry with a resolution of 0.06 $cm^{-1}$ in the wavelength region 240-270 nm. We obtained a high column density of $O_2$ by using a multipass technique (a White cell) as in the previous studies of the Herzberg I band [Yoshino *et al.*, 1994, 1995b]. To observe the weaker Herzberg II and III bands, we increased the $O_2$ pressure to 383 and 766 Torr in the White cell. All observed lines are assigned to those of the three band systems, Herzberg I, II, and III. The absorption of the Herzberg II and III lines we recently recorded are limited by the numbers of molecules. We will make more measurements with more column density by increasing the path lengths in the White cell.

## 2.3 Absorption cross section measurements of $H_2O$ bands in the wavelength region 120-188 nm

Laboratory measurements of the absolute cross sections of $H_2O$ at 295 K have been made throughout the wavelength region 120 nm to 188 nm, using with the 3-m vacuum spectrometer on the BL-20A beam line at the Photon Factory, KEK, Japan. A paper titled "Absorption Cross Section Measurements of Water Vapor in the Wavelength Region 120 nm to 188 nm" has been published in the Chem. Phys. [Yoshino *et al.*, 1996b,1997].

# 3 Publications

## 3.1 Paper Published and in Press (1993-1997)

*Measurements of Absolute Absorption Cross Section of Ozone in the 185-254 nm Wavelength Region and the Temperature Dependence*, K. Yoshino, J.R. Esmond, D.E. Freeman and W.H. Parkinson, J. Geophys. Res. **98**, 5205-5211 (1993).

*Rotational Dependence of Predissociation Linewidths of the Schumann-Runge Bands of Oxygen*, A.S-C. Cheung, D.K-W. Mok, M.J. Jamieson, M. Finch, K. Yoshino, A. Dalgarno, and W.H. Parkinson, J. Chem. Phys., **99**, 1086-1092 (1993).

*Measurements of Absolute Absorption Cross Section of Ozone in the 185-254 nm Wavelength Region and the Temperature Dependence*, K. Yoshino, J.R. Esmond, D.E. Freeman and W.H. Parkinson, J. Geophys. Res. **98**, 5205-5211 (1993).

*The combination of a VUV Fourier Transform Spectrometer and Synchrotron Radiation*, K. Yoshino, P.L. Smith, W.H. Parkinson, A.P. Thorne, and K. Ito, Rev. Scient. Instr. **66**, 2122-2124 (1995).

*Isotopic Dependence of Predissociation Linewidths in the Schumann-Runge Bands of Oxygen*, A.S-C. Cheung, D.K-W. Mok, K. Yoshino, W.H. Parkinson, M.J. Jamieson, A. Dalgarno, and M.S. Child, J. Chem. Phys. **103**, 2369-2371 (1995).

*Absorption Cross Section Measurements of Carbon Dioxide in the Wavelength Region 118.7 nm - 175.5 nm and the Temperature Dependence*, K. Yoshino, J.R. Esmond, Y. Sun, W.H. Parkinson, K. Ito, and T. Matsui, J. Quant. Spectrosc. Radiat. Transf. **55**, 53-60 (1996).

*Molecular Absorption in the VUV by Fourier Transform Spectroscopy*, K. Yoshino, A.P. Thorne, and K. Ito, *Atomic and Molecular Photoionization*, Universal Academic Press, Tokyo, 167-176 (1996).

*The Schumann-Runge Absorption Bands of $O_2$ at 670 K and the Spectroscopic Constants of the Ground State, $X\ ^3\Sigma_g^-$*, A.S-C. Cheung, K. Yoshino, J.R. Esmond, and W.H. Parkinson, J. Molec. Spectrosc. **178**, 66-77 (1996).

*Absorption Cross Section Measurements of Water Vapor in the Wavelength Region 120 nm to 188 nm*, K. Yoshino, J.R. Esmond, W.H. Parkinson, K. Ito, and T. Matsui, Chem. Phys. **211**, 387-391 (1996); **215**, 429-430 (1997).

*Comment on the Herzberg Continuum*, K. Yoshino, D. L. Huestis, and R. W. Nicholls, J. Quant. Spectrosc. Radiat. Transf. (1997), accepted for publication.

## 3.2 Presentations during the period 8/1/96-7/31/97

9/2/96. **Seminar at Laboratoire de Photophysique Moleculaire,** Orsay, France,
Molecular Absorption with the VUV-FT Spectrometer
**K. Yoshino**

9/4-6/96. **Atmospheric Spectroscopy Application Work Shop,** Reims, FRANCE
Molecular Absorption Measurements with VUV Fourier Transform Spectrometer
**K. Yoshino**, A.P. Thorne and K. Ito

2/10-12/97 **Fourier Transform Spectroscopy, Opt. Soc. Am.,** Santa Fe, NM
Measurements of the Schumann-Runge Bands of $O_2$ with VUV-FT Spectrometer and Synchrotron Radiation Source
**K. Yoshino**, J.R. Esmond, W.H. Parkinson, **A.P. Thorne**, J.E. Murray, G. Cox, R.C.M. Learner, K.Ito, T. Imajo, T. Matsui, A.S.-C. Cheung, and K.-S. Leung

4/17/97. **Seminar at The Institute of Physical and Chemical Research,** Wako, Japan
The combination os a VUV Fourier transform spectrometer and synchrotron radiation for Molecular Absorption
**K. Yoshino**

4/18/97. **Seminar at Tokyo Institute of Technology**, Tokyo, Japan
The combination os a VUV Fourier transform spectrometer and synchrotron radiation for Molecular Absorption
**K. Yoshino**

6/10-12/97. **The 20th Annual Review Conference on Atmospheric Transmission Models**, Bedford, MA
The aplication of a VUV-FT spectrometer and sunchrotron radiation source to measurements of $O_2$ and NO molecules
**K. Yoshino**, J.R. Esmond, W.P. Parkinson, A.P. Thorne, J.E. Murray, G. Cox, R.C.M. Learner, K. Ito, T. Imajo, T. Matsui, A.S.-C. Cheung, and K.-S. Leung

6/16/97. **Seminar** AMP. CfA
The aplication of a VUV-FT spectrometer and sunchrotron radiation source to measurements of $O_2$ and NO molecules
**Kouichi Yoshino**

6/16-20/97. **52nd Symposium on Molecular Spectroscopy**, Ohio State University

The application of a VUV-FT spectrometer and synchrotron radiation source to measurement of: I. Predissociated linewidths of the Schumann-Runge bands of $O_2$
**K. Yoshino**, J. R. Esmond, W. H. Parkinson, A. P. Thorne, J. E. Murray, G. Cox, R. C. M. Learner, K. Ito, T. Matsui, T. Imajo, . S.-C. Cheung and K. W.-S. Leung

The application of a VUV-FT spectrometer and synchrotron radiation source to measurement of: II. The $\beta$ (9,0) band of NO
**K. Yoshino**, J. R. Esmond, W. H. Parkinson, A. P. Thorne, J. E. Murray, G. Cox, R. C. M. Learner, K. Ito, T. Matsui, T. Imajo, . S.-C. Cheung and K. W.-S. Leung

Band Oscillator Strengths of the $\tilde{C} - \tilde{X}$ and $\tilde{F}$ - $\tilde{X}$ bands of $H_2O$
**K. Yoshino**, J.R. Esmond, P.L. Smith, K.P. Huber, J.K.G. Watson, K. Ito and T. Matsui

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K. Yoshino, J.E. Murray, J.R. Esmond, Y. Sun and W.H. Parkinson, A.P. Thorne, R.C.M. Learner and G. Cox, (1994), *Fourier Transform Spectroscopy of the Herzberg I Bands of $O_2$*, Can. J. Phys. **72**, 1101-1108.

K. Yoshino, P.L. Smith, W.H. Parkinson, A.P. Thorne, and K. Ito, (1995a), *The combination of a VUV Fourier Transform Spectrometer and Synchrotron Radiation*, Rev. Scient. Instr. **66**, 2122-2124 .

K. Yoshino, J.R. Esmond, J.E. Murray, W.H. Parkinson, A.P. Thorne, R.C.M. Learner and G. Cox, (1995b), *Band Oscillator Strengths of the Herzberg I Bands of $O_2$*, J. Chem. Phys. **103**, 1243-1249.

K. Yoshino, A.P. Thorne, and K. Ito, (1996a), *Molecular Absorption in the VUV by Fourier Transform Spectroscopy*, Atomic and Molecular Photoionization, Universal Academic Press, Tokyo, 167-176.

K. Yoshino, J.R. Esmond, W.H. Parkinson, K. Ito, and T. Matsui, (1996b), *Absorption Cross Section Measurements of Water Vapor in the Wavelength Region 120 nm to 188 nm*, Chem. Phys. **211**, 387-391 ; (1997), **215**, 429-430.