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THE ABSORPTION CROSS SECTIONS OF N_2, O_2, CO, NO, CO_2, N_2O, CH_4, C_2H_4, C_2H_6 AND C_4H_{10} FROM 180 TO 700 Å*

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Abstract—The absorption cross sections of N_2, O_2, CO, NO, CO_2, N_2O, CH_4, C_2H_4, C_2H_6, C_4H_{10} have been measured photoelectrically in the 180–700 Å region using synchrotron radiation. The absorption cross sections in the region $\lambda < 500$ Å was found to be structureless and to increase monotonically with wavelength for all gases. The positions of the structure observed in the 520–720 Å region for N_2, O_2, CO_2 and N_2O are consistent with the various Rydberg series reported by previous authors.

INTRODUCTION

THE ABSORPTION cross sections of simple molecules and hydrocarbon vapors have been reported by several authors.[1–23] Using line emission sources, the absorption cross sections have been measured in the 200–700 Å region either by photographic or photoelectric methods.[1–9] The absorption cross sections have also been measured photoelectrically in the 600–1000 Å region using the Hopfield continuum,[10–21] and in the 300–1000 Å region using synchrotron radiation.[22] REILHAC *et al.*[23] have recently applied the Vodar continuum to measure photographically the absorption cross sections of several gases in the 100–400 Å region. Although the existing absorption cross-section data are extensive, each author has studied only some of the gases presented here, and in limited spectral regions. Here, we present a continuum of cross-section data in the 180–700 Å region for the gases N_2, O_2, CO, NO, CO_2, N_2O, CH_4, C_2H_4, C_2H_6 and C_4H_{10}. The cross sections were measured photoelectrically, using synchrotron radiation produced in the University of Wisconsin Electron Storage Ring.

EXPERIMENTAL

The experimental setup and the technique used to analyze the data have been described in a previous paper.[24] In brief, a grating was used to disperse the synchrotron radiation and a double ionization chamber was used to obtain the cross-section measurements.

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Al and Sn films were used both as optical filters and to separate the ionization chamber from the high-vacuum monochromator. The experimental data were analyzed by a method that assumed that stray light and the second order could be represented at each wavelength by a single absorption coefficient, and the curves of the ratio of ionization currents versus pressure were fitted by adjusting both the cross sections and the relative proportions of true and stray light.

The exit slit of the monochromator was set such that the resolution was approximately 0.5 Å. The gases, supplied by the Matheson Co., Inc., were admitted into a double ionization chamber without further purification. The maximum errors in the cross-section measurements are estimated to be ± 20 per cent of the assigned value in the 170–520 Å and ± 5 per cent in the 520–700 Å region.

RESULTS AND DISCUSSION

(a) *Nitrogen*

Except for recent reports by SASANUMA *et al.*[22] and REILHAC *et al.*[23] all of the previous measurements[1,2,10,11] of the absorption cross section of N_2 have been compiled by HUDSON[25] and will not be reviewed again here. The data of SAMSON and CAIRNS,[1] obtained using a line emission source, are compared with the present results and both are shown in Fig. 1. The Rydberg states identified by CODLING[26] for the $N_2^+(C^2\Sigma_u^+)$ state and by OGAWA and TANAKA[27] for the $N_2^+(B^2\Sigma_u^+)$ state are also indicated in the figure. The structure may extend further toward the region of $\lambda < 520$ Å but, since it is in the Al film region, it may be masked somewhat by second order and stray light. The photoionization cross section of N_2 from 500–650 Å calculated by TUCKWELL,[28] who used two-center coulomb waves for the final electronic states, is higher than the present measurements by a factor of two.

The purity of the gas was 99.99 per cent.

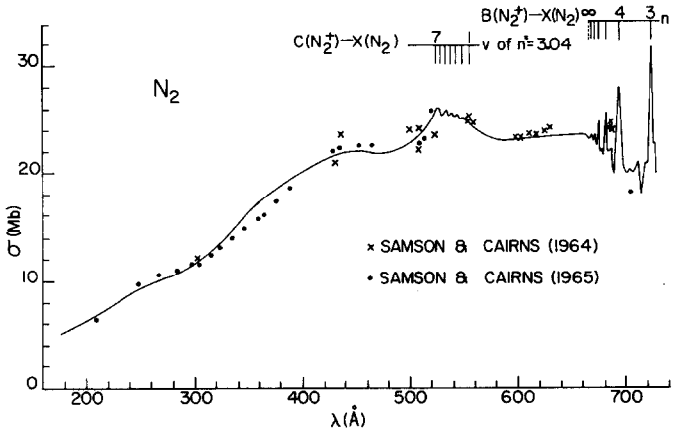

FIG. 1. The absorption cross section of nitrogen. X and • indicate the data given by Samson and Cairns in 1964 and 1965, respectively. The positions of the Rydberg levels for the $N_2^+(B\,^2\Sigma_u^+)$ and $N_2^+(C\,^2\Sigma_u^+)$ states identified by Ogawa and Tanaka and by Codling, respectively, are also indicated.

(b) *Oxygen*

Again, except for the reports of SASANUMA *et al.*[22] and REILHAC *et al.*,[23] the previous cross-section results[1,2,10,12,13] on O_2 have been compiled by HUDSON.[25] As above, only SAMSON and CAIRNS' data[1] were adopted to compare with the present results, shown in Fig. 2. The Rydberg states assigned by CODLING and MADDEN[29] to the $O_2^+(c\,^4\Sigma_u^-)$ state, and by YOSHINO and TANAKA[30] to the $O_2^+(B\,^2\Sigma_g^-)$ and $O_2^+(b\,^4\Sigma_g^-)$ states, are indicated in the figure to identify the observed structure. As in the case of N_2, the structure may extend further toward the region of $\lambda < 520$ Å since second order and stray light obscure weak features.

The purity of the gas was 99.99 per cent.

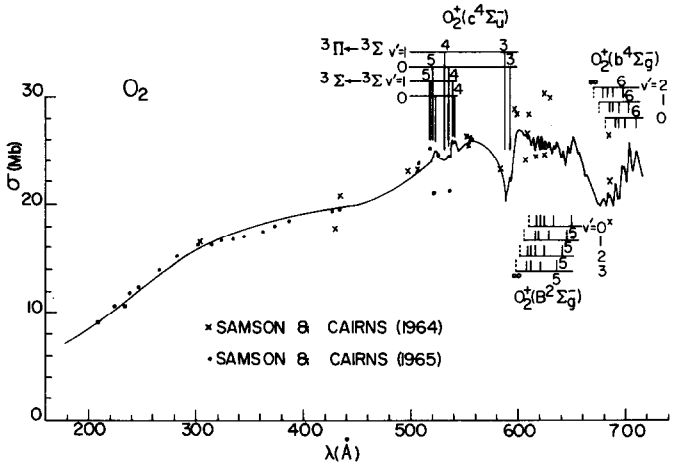

FIG. 2. The absorption cross section of oxygen. X and • indicate the data given by Samson and Cairns in 1964 and 1965, respectively. The positions of the Rydberg states for the $O_2^+(c\,^4\Sigma_u^-)$ states identified by Codling and Madden and the $O_2^+(B\,^2\Sigma_g^-)$ and $O_2^+(b\,^4\Sigma_g^-)$ states identified by Yoshino and Tanaka are also indicated.

(c) *Carbon monoxide*

The absorption cross section of CO has been measured by several authors.[3,4,14,15,22,23] Previous results are reviewed in the compilation by HUDSON[25] while new measurements have been recently reported by SASANUMA *et al.*[22] and REILHAC *et al.*[23] The present results are shown in Fig. 3. The results of CAIRNS and SAMSON[3] are again indicated in the figure for comparison. For $\lambda < 500$ Å, the present results are consistently lower than those of CAIRNS and SAMSON.[3] Considering the possible errors claimed by both measurements, these two sets of data are not in conflict. In the 625–660 Å region, there are Rydberg series leading to the $CO^+(B^2\Sigma^+)$ state,[31] but they are too weak to be observed with certainty in the present measurements.

The purity of the gas was 99.5 per cent.

(d) *Nitric oxide*

The absorption cross section of NO below 600 Å has not previously been investigated with a continuum background, except for the limited measurements of REILHAC *et al.*[23] These data, in addition to those of METZGER *et al.*,[6] WATANABE *et al.*[17] and SUN and

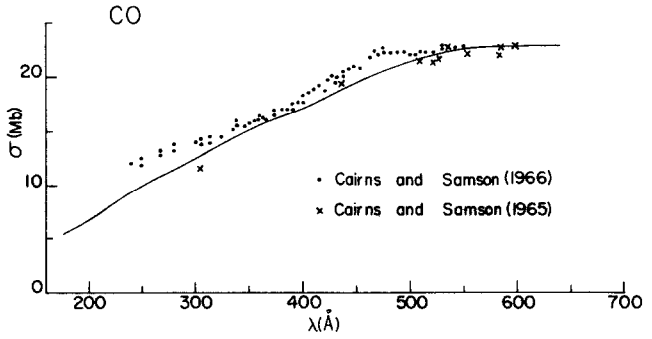

FIG. 3. The absorption cross section of carbon monoxide. X and • indicate the data given by Cairns and Samson in 1965 and 1966, respectively.

WEISSLER,[5] were used for comparison with the present results and are shown in Fig. 4. No structure was observed in the present measurement region.

Since NO is a very active gas and may react with the impurity molecules trapped on the surfaces inside the ionization chamber, the impurity percentage may be greater than that of the bottled gas so that the experimental error may be somewhat higher than for the other gases. The purity of the supplied gas was 99.8 per cent.

(e) *Carbon dioxide*

The absorption cross section of CO_2 has been intensively measured[2–4,18,19,23] in the past few years. For $\lambda < 600$ Å, there exist controversial results which have been discussed by HUDSON.[25] The data of CAIRNS and SAMSON[3] were adopted to compare with the present results and are shown in Fig. 5. The positions of Rydberg states leading to the $CO_2^+(B\,^2\Sigma_u^+)$ and $CO_2^+(C\,^2\Sigma_g^+)$ states, as assigned by TANAKA *et al.*[32] and TANAKA and OGAWA,[33] were used to identify the structure in the 640–740 Å region.

The purity of the gas was 99.8 per cent.

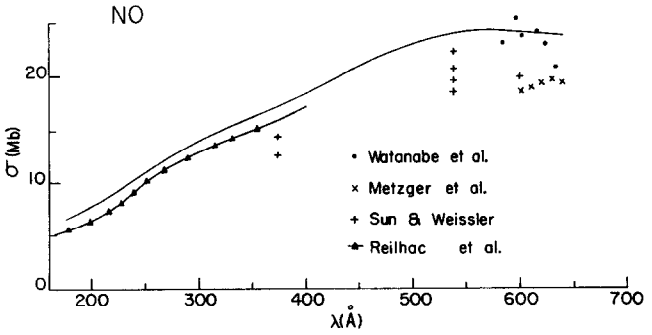

FIG. 4. The absorption cross section of nitric oxide. The data given by Watanabe *et al.* are represented by •, Metzger *et al.* by X, and Reilhac *et al.* by △.

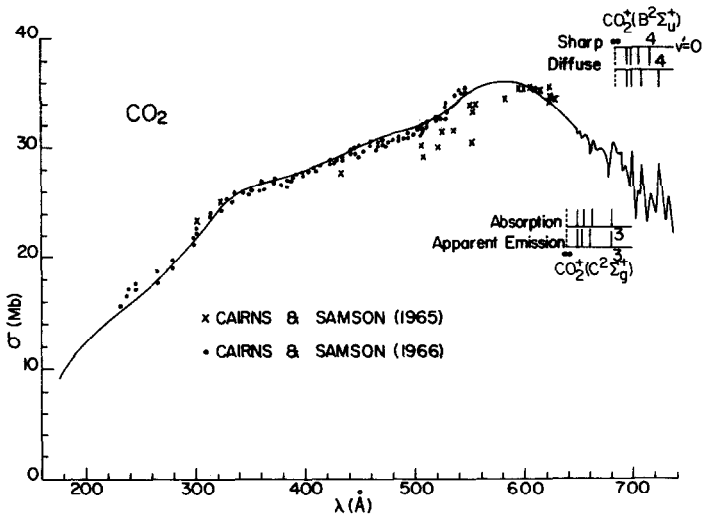

FIG. 5. The absorption cross section of carbon dioxide. X and • present the data given by Cairns and Samson in 1965 and 1966, respectively. The positions of the Rydberg states for the $CO_2^+(B\ ^2\Sigma_u^+)$ and $CO_2^+(C^2\Sigma_g^+)$ states identified by Tanaka *et al.* and by Tanaka and Ogawa are also indicated.

(f) *Nitrous oxide*

In the wavelength region below 600 Å, the absorption cross section of N_2O has only been measured by Reilhac *et al.* In the region from 600–720 Å, it has only been measured by COOK *et al.*[20] Both of their results were used to compare with the present measurements and are shown in Fig. 6. The positions of the Rydberg absorption series VI and VII and the apparent emission series VIII and IX, as given by TANAKA *et al.*,[34] are also indicated in the figure to identify the structure.

The purity of the gas was 98 per cent.

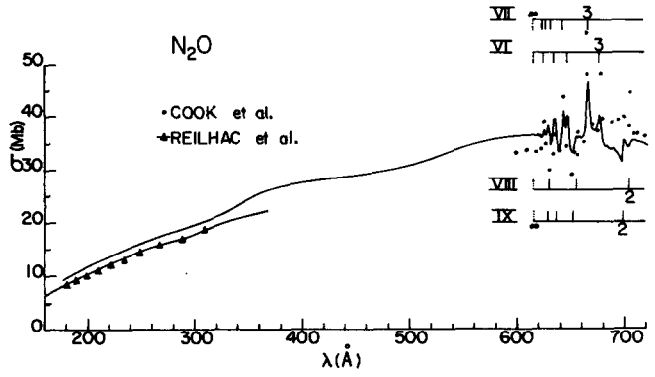

FIG. 6. The absorption cross section of nitrous oxide. A • indicates the data given by Cook *et al.*, and a ▲ by Reilhac *et al.* The positions of the Rydberg states of the absorption series VI and VII and the apparent emission series VIII and IX given by Tanaka *et al.* are also indicated.

(g) *Methane*

Because of its theoretical interest,[35] the absorption cross section of CH_4 in the presently investigated region has been measured by a number of investigators.[2,6–8,21,23] The data given by WAINFAN *et al.*,[2] DITCHBURN,[6] RUSTGI,[7] LUKIRSKII *et al.*[8] and METZGER and COOK[21] have been used to compare with the present results, shown in Fig. 7. No structure was observed in the present data.

The purity of the gas was 99 per cent.

(h) *Ethylene*

There are few data on the absorption cross section of C_2H_4 in the present region of investigation. The only available data are given by SCHOEN[9] and METZGER and COOK[21] and were used to compare with the present results, shown in Fig. 8. No structure was observed.

The purity of the gas was 99.5 per cent.

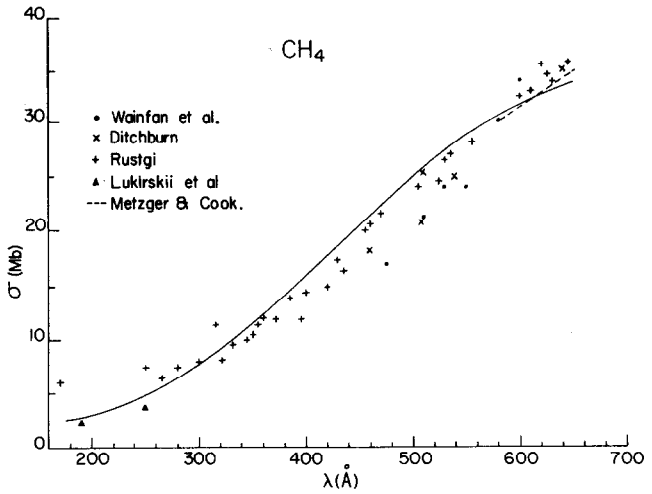

FIG. 7. The absorption cross section of methane. A • indicates the data given by Wainfan *et al.*, X by Ditchburn, + by Rustgi, Δ by Lukirskii *et al.* and − − − by Metzger and Cook.

(i) *Ethane*

Just as for C_2H_4, the absorption cross section of C_2H_6 in the presently investigated spectral region has been measured only in limited spectral regions by SCHOEN[9] and METZGER and COOK.[21] Their data are compared with the present results in Fig. 9. No structure was observed.

The purity of the gas was 99 per cent.

(j) *Butane*

The absorption cross section of C_4H_{10} in the spectral region from 180–650 Å has been previously investigated only at a limited number of wavelengths by SCHOEN.[9] His data

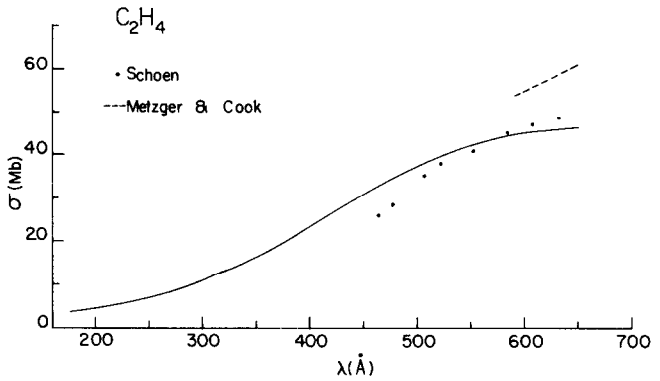

FIG. 8. The absorption cross section of ethylene. A • and − − − indicate the data given by Schoen and by Metzger and Cook, respectively.

were used to compare with the present results and are shown in Fig. 10. No structure was observed.

The purity of the gas was 99.5 per cent.

SUMMARY

The absorption cross sections of N_2, O_2, CO, NO, CO_2, N_2O, CH_4, C_2H_4, C_2H_6 and C_4H_{10} have been measured and agree best with the previous data obtained using line emission sources.

Comparing the presently measured absorption cross sections, it was found that various gases have a common feature in the structureless region. The absorption cross sections increase monotonically with wavelength for all gases, with the cross sections of the group consisting of N_2, O_2, CO, NO, CO_2 and N_2O increasing at a rate different from those of CH_4, C_2H_4, C_2H_6 and C_4H_{10}. The absorption cross sections of the former group increase rapidly from 180 Å toward the longer wavelength, and reach a relatively flat portion for the

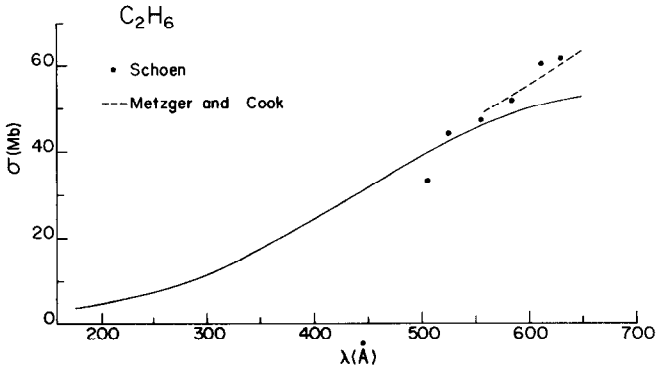

FIG. 9. The absorption cross section of ethane. A • and − − − indicate the data given by Schoen and by Metzger and Cook, respectively.

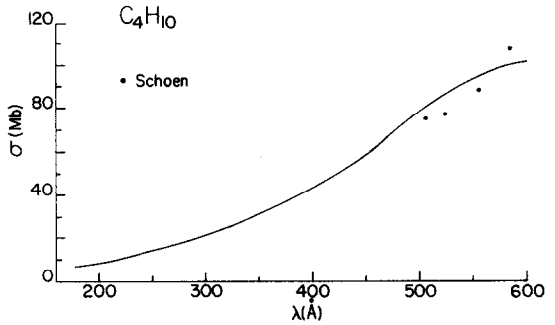

FIG. 10. The absorption cross section of butane. The data given by Schoen are indicated by a •.

region $\lambda < 400$ Å. The absorption cross sections of the latter group increase slowly but steadily from 180 Å toward the longer wavelength region.

The previously known structure of N_2, O_2, CO_2 and N_2O is observed in the tin film region (520–720 Å). The positions of the structure are consistent with the various Rydberg series reported by previous authors.

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