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DESY SR-73/4
March 1973

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by

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The Formation of Excited CO_2^+ Ions by Vacuum Ultraviolet Radiation

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Excited CO_2^+ ions are formed by irradiating CO_2 molecules with the synchrotron radiation. The excitation function of CO_2^+ $(\tilde{B}^2\Sigma_u^+)$ shows a pronounced structure which can be explained by an interaction of the Rydberg states $np\pi_u$ converging to $\tilde{C}^2\Sigma_g^+$ with the continuum of $\tilde{B}^2\Sigma_u^+$.

The formation of excited CO_2^+ ions by photon molecule reaction is of special interest in the physics of planetary atmospheres[1]. In order to study the excitation mechanism we have used the synchrotron radiation as a primary light source. The light intensity of the synchrotron at the exit slit of the first monochromator amounted to 10^9 photons/Å sec at about 600 Å. (This value is related to a beam current of the accelerator of 30 mA). Towards 400 Å the intensity drops down to approximately 10^8 photons/Å sec[2]. The wavelength resolution was about 3.5 Å. The pressure within the collision chamber was varied between 10^{-3} torr and $5 \cdot 10^{-2}$ torr.

The fluorescence radiation was observed with a second monochromator which had a wavelength resolution of about 20 Å in the region from 2000 Å to 4000 Å. The signal was detected with a cooled multiplier (type EMI 6256 S).

Submitted to Physics Letters A

Fig. 1 shows the emission spectrum of CO_2 which was obtained at a primary photon energy of 19 eV. The radiation components can be classified according to ref. 3. The vibrational structure with Δv constant is not resolved. For example the component designated by 2,0,0 - 0,0,0 contains the transitions 3,0,0 - 1,0,0 , 4,0,0 - 2,0,0 and 5,0,0 - 3,0,0. A similar picture was obtained by measuring the spectrum of the Martian atmosphere[1].

Fig. 2 gives the excitation function of the transition $\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g$ at about 2900 Å. We have found a sharp structure at 679 Å and 662.5 Å.

The electron configuration of the ground state of CO_2 can be written as

$$KKK \underbrace{(\sigma_g)^2\ (\sigma_u)^2}_{a}\ \underbrace{(\sigma_g)^2\ (\sigma_u)^2}_{b}\ (\pi_u)^4\ (\pi_g)^4\quad {}^1\Sigma_g^+ \quad [4].$$

The removal of a nonbonding σ_u electron of type b results in the state $\tilde{B}^2\Sigma_u^+$ of the ion. On the other hand one gets a Rydberg series converging to the state $\tilde{C}^2\Sigma_g^+$ if a σ_g electron of the same type is raised to a $np\pi_u$ orbital[5].

This apparent emission series is well known from absorption measurements[6].

Since the window structure at 679 Å and 662.5 Å in the excitation function of $\tilde{B}^2\Sigma_u^+$ coincides, with respect to energy, with the states $4p\pi_u$ and $5p\pi_u$ we conclude that it is due to an interaction of the Rydberg states with the continuum corresponding to $\tilde{B}^2\Sigma_u^+$. This interpretation is strengthened by the fact that we have found a similar structure in N_2O (to be published). A window structure in N_2O was found by ref. 7 who measured the total fluorescence with four filters.

We would like to thank our colleagues of the Synchrotron Radiation Group at DESY for valuable help in our experimental work. Especially we are indebted to the Munich Group for making available to us their monochromator.

References

1) C.A. Barth, C.W. Hord, J.B. Pearce, K.K. Kelly, G.P. Anderson, and A.I. Stewart, J. Geophys.Res.76, 2213(1971)

2) U. Backhaus, Diplomarbeit, II. Institut für Experimentalphysik der Universität Hamburg, Hamburg, Germany

3) T.S. Wauchop and H.P. Broida, J. Geophys.Res.76, 21(1971)

4) D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, Molecular Photoelectron Spectroscopy, A Handbook of He 584 Å Spectra, Wiley-Interscience, London (1970)

5) E. Lindholm, Ark.Fys.40, 125(1969)

6) Y. Tanaka, A.S. Jursa, and F.J. LeBlanc, J.Chem.Phys.32, 1199(1960)

7) G.R. Cook, P.H. Metzger, and M. Ogawa, J.Opt.Soc.Am.58, 129(1968)

Figure Captions

Fig. 1 Emission spectrum of CO_2^+ obtained by irradiating CO_2 with 19 eV photons. The dotted part of the spectrum is taken from another measurement.

Fig. 2 Photoexcitation function of the transition CO_2^+ ($\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g$).

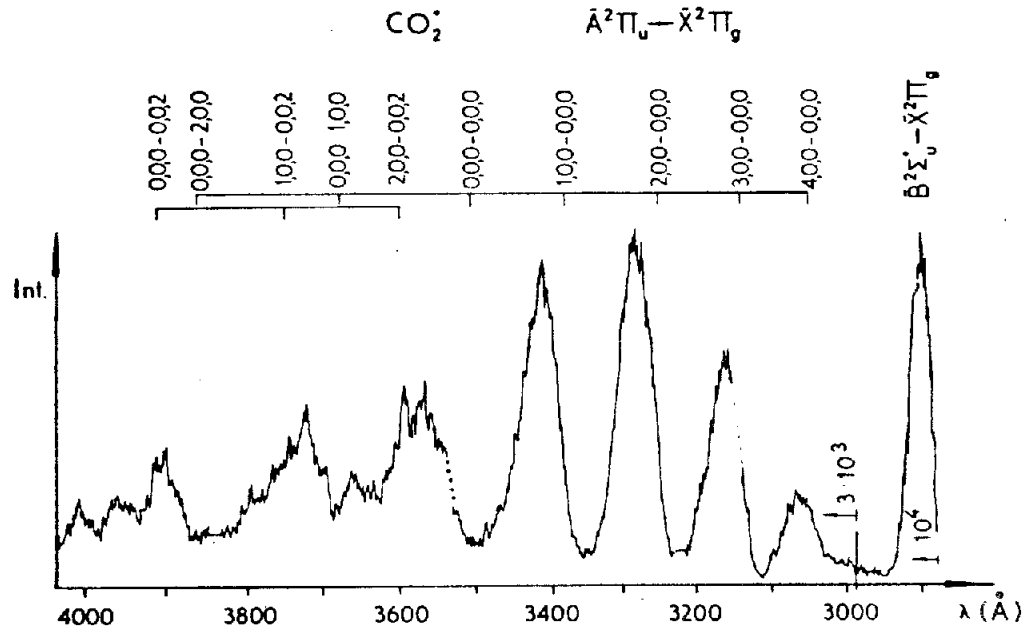
CO_2^+ $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$
0,0,0-0,0,2
0,0,0-2,0,0
1,0,0-0,0,2
0,0,0 1,0,0
2,0,0-0,0,2
0,0,0-0,0,0
1,0,0-0,0,0
2,0,0-0,0,0
3,0,0-0,0,0
4,0,0-0,0,0
$\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g$
Int.
$3 \cdot 10^3$
$1 \cdot 10^4$
4000
3800
3600
3400
3200
3000
λ (Å)

Fig. 1

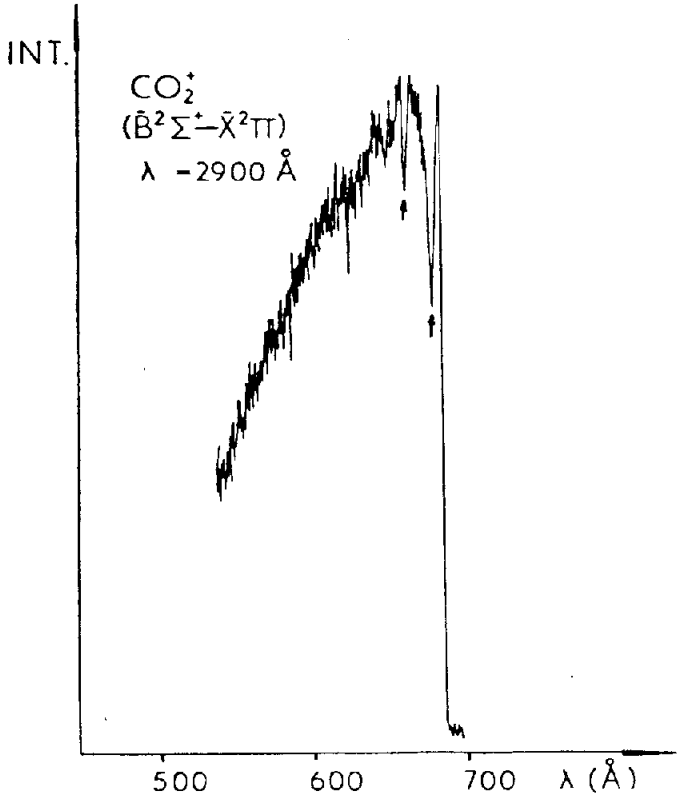
INT.
CO_2^+
$(\tilde{B}^2\Sigma^+ - \tilde{X}^2\Pi)$
λ -2900 Å
500
600
700
λ (Å)

Fig. 2