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ENERGY TRANSFER IN PLANETARY ATMOSPHERES: OPTICAL SPECTROSCOPIC STUDIES

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FORWARD

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ABSTRACT

Several different cross sections have been measured in the laboratory for the production of electronically excited species that are observed in the atmospheres of the planets. Spectra of CO_2^+ ($\tilde{A}\ ^2\Pi - \tilde{X}^2\Pi$) and ($\tilde{B}^2\Sigma - \tilde{X}^2\Pi$) band systems produced by the interaction of CO_2 with $He(2^3S)$ metastable atoms are similar to spectra observed in the atmosphere of Mars. Experimental transition probabilities of the CO_2^+ ($\tilde{A} - \tilde{X}$) band system produced by this energy transfer process were measured using spectra with 0.02 nm resolution. Recombination of the resultant CO_2^+ gave large concentrations of $CO(a\ ^3\Pi)$. Decay of CO ($a^2\Pi - X^1\Sigma$) Cameron bands in a flow tube allowed a measurement of the lifetime of the CO metastable. Also removal of the $CO(a\ ^3\Pi)$ from a flowing afterglow gave quenching rates for N_2, NO, and CO_2. Spectroscopic emission from the interaction of 58.4 nm photons with N_2, O_2, CO, NH_3, and N_2O has been compared with the photon interaction with CO_2. Absolute cross sections were measured for the production of each vibrational level of all observed electronically excited states. Helium metastable atoms have been used to produce metastable $CS(a\ ^3\Pi)$ by the interaction of CS_2 with a helium afterglow.

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PART I

INTRODUCTION

Techniques of optical spectroscopy have been applied to understanding planetary atmospheres. A variety of reaction systems such as discharges, active afterglows and flames have been used for this purpose. The program has had as a main purpose the teching of techniques of optical spectroscopy as applied to atmospheric studies. In addition, graduate students and postdoctoral fellows were able to do research at Ames Research Center and at the Molecular Physics Laboratories at U.C.S.B., doing spectroscopy studies relevant to the upper atmospheres of Mars, Venus, Jupiter, and Earth.

PART II

WORK AT U.C.S.B.

T. S. Wauchop

Flowing afterglows in rare gases have become a useful tool for study of rare gas metastable atoms and ions and of various energy transfer processes. Comprehensive discussions of these afterglows are given by Ferguson;[1] Bell, Dalgarno, and Kingston;[2] and Stedman and Setser.[3] These rare gas afterglows are produced in several ways, including microwave[4] and direct-current[5] discharges and electron bombardment.[6,7]

In the helium afterglow, several helium species, He^+, $He(2^3S)$, $He(2^1S)$, $He_2(^2\Sigma)$, and He_2^+ in addition to ground state $He(1^1S)$, have been detected. Metastable $He(2^1S)$ atoms are rapidly converted to $He(2^3S)$ by elastic collisions with electrons.[8] Ionic products can be removed by using microwave heating[9] or by addition of an electron scavenger such as SF_6.[10] There is little production of metastable molecular helium, $He_2(2^3S)$, in afterglows at pressures below 10 torr.[9] It is, therefore, possible to produce an afterglow in which $He(2^3S)$ is the dominant energetic species.

When $He(2^3S)$ interacts with a diatomic or triatomic molecule, its electronic excitation energy can be transferred to electronic and vibrational excitation of the molecule. Using the flowing afterglow system shown in Fig. 1, we have measured the rates of production of electronically excited molecules observed spectroscopically between 190 and 750 nm in the reaction of $He(2^3S)$ with CO_2. Table I gives the production rates for CO_2^+ $\tilde{A}\ ^2\Pi$ and $\tilde{B}\ ^2\Sigma$ and CO $X\ ^1\Pi$ and $b\ ^3\Sigma$. Using spectra similar to the one shown in Fig. 2, we obtained the photon transition probabilities for the CO_2^+ $\tilde{A} - \tilde{X}$ band system

given in Table II.

Observation of the CO Cameron band ($a^3\Pi - x^1\Sigma$) in the atmosphere of Mars[10] has lead to an increase in interest in possible production process of CO($a\ ^3\Pi$). Recently several new measurements have been made of the lifetime of the metastable state.[11,12,13,14] Measurements have been made of collisional deactivation rates of CO($a\ ^3\Pi$) with various atmospheric gases.[12]

One possible method proposed for the production of CO($a\ ^3\Pi$) in the Martian atmosphere was the dissociative recombination of CO_2^+.[15] We have produced high concentrations of CO_2^+ by He(2^3S) interaction with CO_2. Spectra taken in this system confirmed the production of CO($a\ ^3\Pi$) (see Fig. 3).

Decays of the CO metastable in the flow tube were used to measure the radiative lifetime and quenching rates. The value of the lifetime measured in this manner was 7 ± 4 msec. Measured quenching rates and cross sections for the reactions of CO($a\ ^3\Pi$) with N_2, NO, CO_2, and He are given in Table III. An estimate of the recombination rate of CO_2^+ also was obtained. It was found to be between 8.5 and 20×10^{-7} cm^3 sec^{-1}, within an order of magnitude of published values.[16]

Quenching of CO($a\ ^3\Pi$) by NO was found to produce NO A $^2\Sigma$ and B $^2\Pi$; relative production efficiencies for each vibrational level are given in Table IV.

By estimating losses of CO($a\ ^3\Pi$) due to diffusion and quenching, we found that in order to account for the intensities of the Cameron bands observed more than 50% of the CO_2^+ present must give CO($a\ ^3\Pi$) on recombination.

K. Monahan

Recent space probes and satellites have increased interest in the effects of solar radiation on gases found in planetary atmospheres. Laboratory studies of 58.4 nm photon interaction on CO_2 [17] were carried out as a result of Mariner probes to Mars.[18] Ground-based and satellite studies of the earth's upper atmosphere make it desirable to further understand the interaction of prominent solar emission features[19] on gases such as N_2 and O_2. The proposed "grand tour" of the outer planets will probably show spectra produced by the interaction of solar radiation on NH_3 and CH_4 in the atmosphere of Jupiter.

Commercial production of thin aluminum filters that pass wavelengths between 30 and 70 nm have made it possible to produce an intense 58.4 nm light source in the laboratory. Using the previously described experimental arrangement,[17] we have obtained relative production cross sections for the interaction of 58.4 nm photons with N_2, O_2, CO, N_2O, and NH_3. Interaction with CH_4, C_2H_5, NO_2, and H_2O gave no emission in the wavelength range between 200 and 750 nm.

Using the absolute cross section for production of the CO_2^+ $(\tilde{A} - \tilde{X})$ band system by photoionization of CO_2 at 58.4 nm[17] as a standard, absolute cross sections for the production of each detected band system were measured. Relative populations of each vibrational level observed were calculated from intensities using the relation,[20]

$$I_{v'v''} \propto N_{v'} q_{v'v''} \nu^3 . \qquad (1)$$

They are given in Table V along with absolute cross sections for the production of each vibrational level.

J. West

Production of $CO(a\ ^3\Pi)$ from CO_2^+ suggests that CS_2^+ recombination may produce $CS(a\ ^3\Pi)$. Addition of CS_2 to a $He(2^3S)$ afterglow produces a green flame. Spectra of this flame show band systems in the green region of the spectrum that are as yet unidentified and bands of CS $(a^3\Pi - x^1\Sigma)$.[21] Production of a $CS(a\ ^3\Pi)$ afterglow similar to the $CO(a\ ^3\Pi)$ afterglow described earlier in this report provides a good experimental situation to study the properties of the CS metastable.

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TABLE I Yields of CO_2^+ $(\tilde{A} - \tilde{X})$ and $(\tilde{B} - \tilde{X})$ and CO (b − a) and (A − X) in the reaction of $He(2^3S)$ with CO_2 with a flux = 1.31×10^{15} $He(2^3S)$ sec^{-1}.

Molecule	Band System	Intensity (photons sec^{-1})	Production efficiency	k (cm^3 sec^{-1})	σ (cm^2)
CO_2^+	$\tilde{A}\ ^2\Pi - \tilde{X}\ ^2\Pi$	$(320 \pm 150) \times 10^{12}$	0.25	$(1.7 \pm 0.9) \times 10^{-10}$	$(11 \pm 5) \times 10^{-16}$
	$\tilde{B}\ ^2\Sigma - \tilde{X}\ ^2\Pi$	(210 ± 100)	0.16	1.1 ± 0.5	7 ± 4
CO	$b\ ^3\Sigma - a\ ^3\Pi$ (3rd positive)	6	0.004	0.03	0.25
	$A\ ^1\Pi - X\ ^1\Sigma$ (4th positive)	30	0.02	0.13	1

TABLE II Transition probabilities of CO_2^+ $\tilde{A} - \tilde{X}$ measured from 0.02 nm resolution spectra. Figures with brackets are for the (v',0,0) → (v',0,2) transitions and those without brackets for (v',0,0) → (v",0,0).

(a) J = 3/2

v' \ v"	0	1	2	3	4
0	0.31 (0.10)	0.22 (0.19)	0.14	0.02	0.01
1	0.60 (0.01)	0.06 (0.03)	0.06 (0.07)	0.18	
2	0.49 (0.01)	0.15 (0.03)	0.20 (0.01)	(0.06)	0.05
3	0.19	0.35 (0.04)	0.14	0.12 (0.09)	0.02 (0.05)
4	0.13	0.17	0.48 (0.04)	0.06	0.12
5		0.51	0.35	0.13	

(b) J = 1/2

v' \ v"	0	1	2	3	4
0	0.24 (0.10)	0.25 (0.24)	0.11	0.05	0.02
1	0.51 (0.07)	0.04 (0.04)	0.13	0.14	0.06
2	0.46 (0.03)	0.10 (0.07)	0.20 (0.02)	0.05 (0.03)	0.04
3	0.48	0.18 (0.10)	0.03 (0.05)	0.10 (0.05)	0.01
4	0.17	0.54	0.05 (0.07)	0.07	0.10
5		0.52	0.35	0.13	

TABLE III Quenching rates of CO_2, N_2, He, and NO on CO($a\ ^3\Pi$).

Reactant		k ($cm^3\ sec^{-1}$)	σ (cm^2)
NO		$3.2 \pm 1.6 \times 10^{-10}$	$4.9 \pm 2.4 \times 10^{-16}$
N_2	$v' = 0$	3.8 ± 1.9	5.7 ± 2.8
	$v' \geq$	7.3 ± 3.6	11 $\pm$ 5.0
CO_2		4.8 ± 2.4	7.9 ± 4.0
He		$< 10^{-13}$	$< 7 \times 10^{-19}$

TABLE IV Relative populations of NO $A\ ^2\Sigma$ and $B\ ^2\Pi$ produced in the reaction of CO($a\ ^3\Pi$) with NO($x\ ^2\Pi$).

Electronic Level	v'	Relative Population
$A\ ^2\Sigma$	0	1.00
	1	0.12
	2	0.05
$B\ ^2\Pi$	0	0.16
	1	0.10

TABLE V

Added Gas	Observed Bands	v'	Relative Population	Cross Section ($\times 10^{-18}$ cm^2)
N_2O	N_2O^+ ($A^2\Sigma - X\ ^2\Sigma$)	0	1.0	9.2
		1	0.08	0.9
N_2	N_2^+ ($B^2\Sigma - X^2\Sigma$)	0	1.0	4.7
		1	0.06	0.28
O_2	O_2^+ ($b^4\Sigma - a^4\Pi$)	0	1.0	1.0
		1	0.42	0.38
		2	0.12	0.10
CO	CO^+ ($B^2\Sigma - X^2\Sigma$)	0	1.0	0.66
		1	0.75	0.67
		2	0.73	0.68
CO	CO^+ ($A^2\Pi - X^2\Sigma$	0	0.78	0.91
		1	0.93	1.8
		2	1.0	2.1
		3	0.22	0.73
		4	0.17	0.68
		5	0.16	0.58

FIGURE CAPTIONS

Fig. 1a Side view of the reaction chamber used to study the $He(2^3S)$ and CO_2 flame including the He afterglow region.

1b Top view of the reaction chamber for studying the $He(2^3S)$ and CO_2 flame, and thelamp and optics used to measure $H(2^3S)$ concentration.

Fig. 2 A 0.02 nm resolution spectrum of CO_2^+ ($\tilde{A}^2\Pi - \tilde{X}^2\Pi$) between 320.0 and 365.0 nm as seen in a CO_2 – $He(2^3S)$ flame. Similar spectra were used to obtain the transition probabilities of CO_2^+ ($\tilde{A} - \tilde{X}$) in Table I.

Fig. 3 Spectrum of CO ($a^3\Pi - x^1\Sigma$) Cameron bands observed in recombination of CO_2^+ with electrons (0.02 nm resolution).

FIG. 1

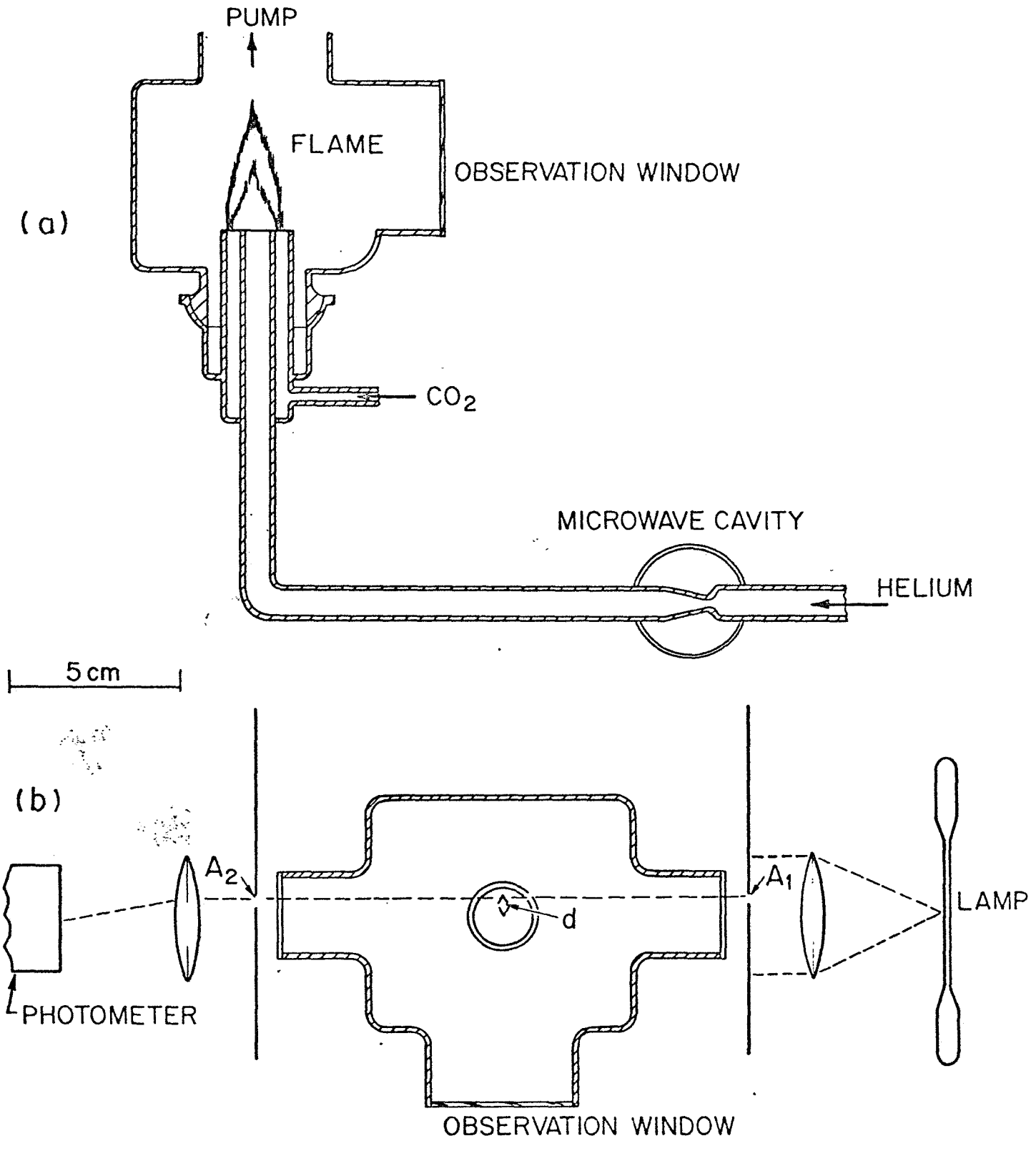

PUMP
FLAME
OBSERVATION WINDOW
(a)
CO_2
MICROWAVE CAVITY
HELIUM
5 cm
(b)
A_2
A_1
d
LAMP
PHOTOMETER
OBSERVATION WINDOW

FIG. 2

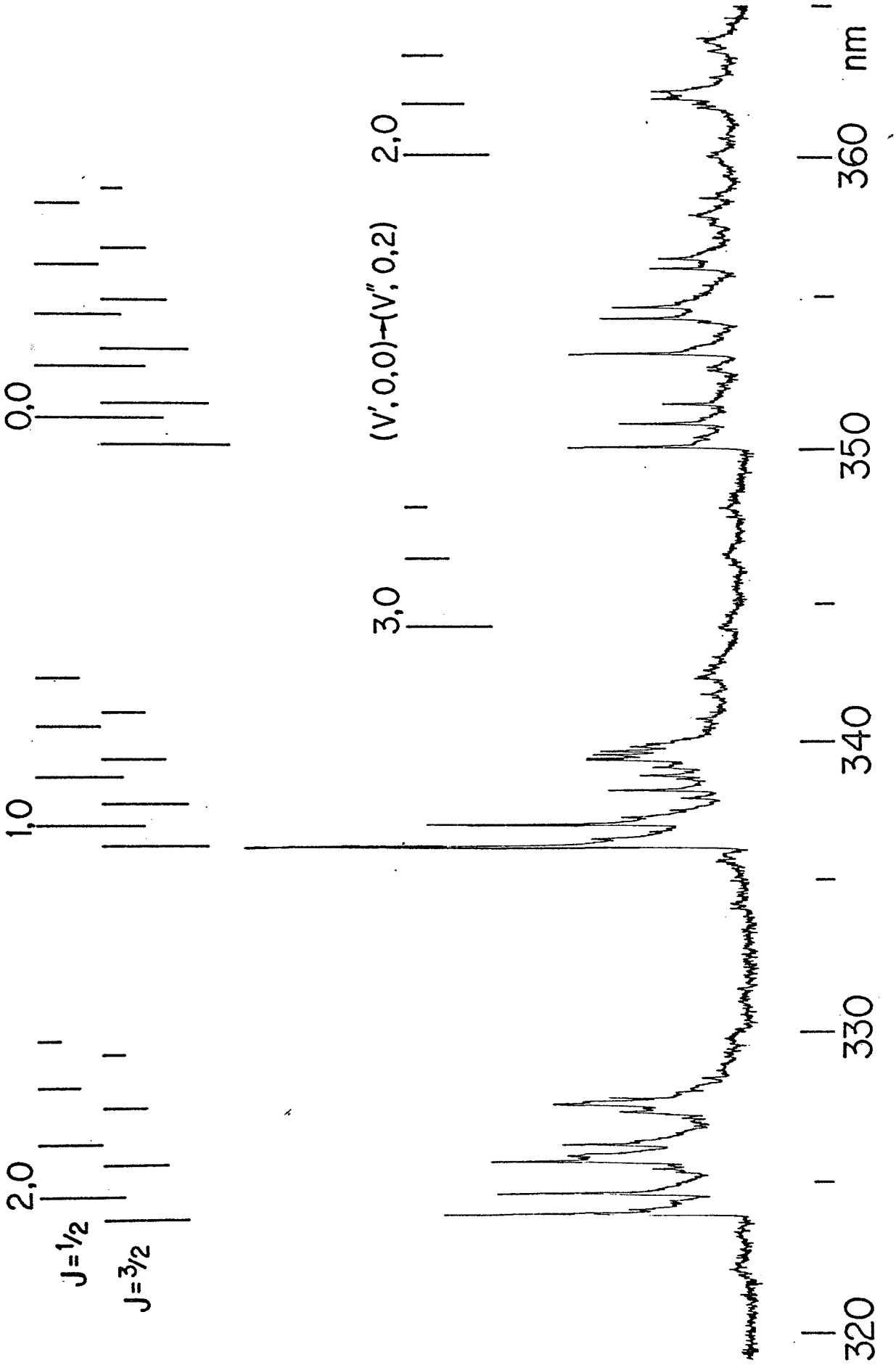
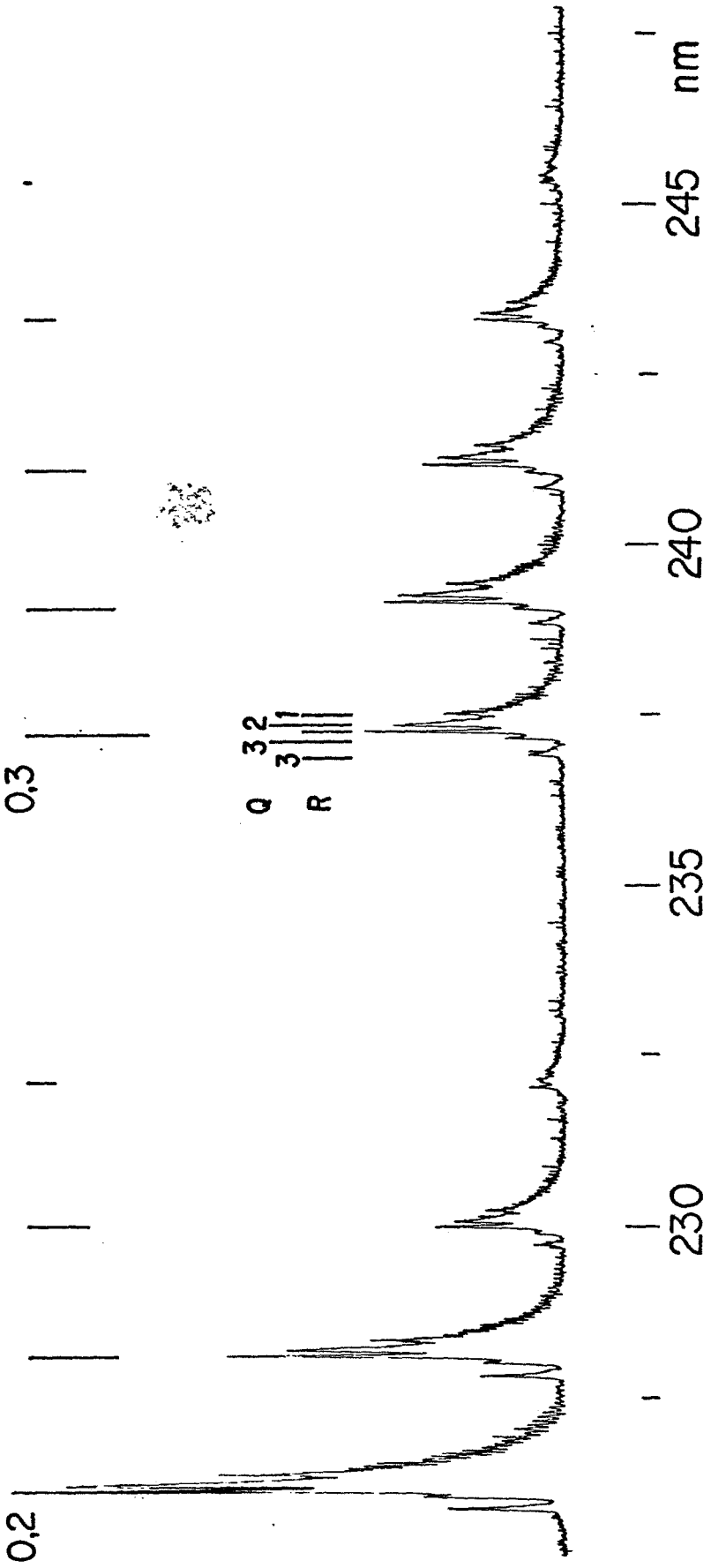


FIG. 3



APPENDIX A

INVITED LECTURES AND PAPERS

12/ 1/70 Seminar, Department of Physics, U.C.S.B.
"Outsider's View of the Ultraviolet Spectrum of Mars" (H. P. Broida)

1/28/71 Western Spectroscopy Association Conference, Asilomar, California
"Ultraviolet Spectra of Mars" (H. P. Broida)

3/11/71 Fifth Arizona Conference on Planetary Atmospheres, Tucson, Arizona
"Cross Sections for the Production of Fluorescence of CO_2^+ in the Photoionization of CO_2^+ by 58.4 nm Radiation" (T. S. Wauchop)

3/13/71 Seminar, Department of Physics, U.C. Irvine
"Ultraviolet Spectra of Mars" (H. P. Broida)

6/14/71 Molecular Spectroscopy Symposium, Columbus, Ohio
"Lifetime and Quenching of $CO(a\ ^3\Pi)$ in a Flowing Helium Afterglow" (T. S. Wauchop)

PUBLISHED ARTICLES

Author	Title	Journal
T. S. Wauchop H. P. Broida	Absolute Measurements of Light Emission from CO_2^+ in the Interaction of $He(2^3S)$ with CO_2	J. Quant. Spectrosc. Radiat. Transfer (In press)
T. S. Wauchop H. P. Broida	Lifetime and Quenching of $CO(a\ ^3\Pi)$ Produced by Recombination of CO_2 Ions in a Helium Afterglow	In preparation
K. Monahan T. S. Wauchop H. P. Broida	Cross Section Studies of Spectral Emission Produced by Interaction of 58.4 nm Radiation with N_2, CO, O_2, N_2O and NH_3	In preparation
T. S. Wauchop	Fluorescence of CO_2^+ in the Photoionization of CO_2 by 58.4 nm Radiation	J. Atmos. Sciences (In press)