Pulsed Field Ionization-Photoelectron Study of CO_2^+ ($X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$, and $C^2\Sigma_g^+$) in the Energy Range of 13.6-20.0 eV

J.B. Liu[1], W.W Chen[1], C.-W. Hsu[1], M. Hochlaf[2], M. Evans[3], S. Stimson[3], and C. Y. Ng[3]

[1]Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA

[2] Theoretical Chemistry Group, University of Marne-La-Vallée, F-77454 France

[3]Ames Laboratory, USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

INTRODUCTION

The vacuum ultraviolet pulsed field ionization-photoelectron (PFI-PE) spectra for CO_2 have been measured in the full energy range of 13.6-20.0 eV, revealing complex vibronic structures for the CO_2^+($X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$ and $C^2\Sigma_g^+$) states. In the spectrum for CO_2^+($X^2\Pi_g$), vibronic bands involving excitations of the symmetric stretching (ν_1^+) mode, the asymmetric stretching (ν_3^+) mode, and Renner-Teller components associated with excitation of the bending (ν_2^+) mode are identified. The PFI-PE spectra for CO_2^+($A^2\Pi_u$, $B^2\Sigma_u^+$, and $C^2\Sigma_g^+$) are dominated by the ν_1^+ vibrational progressions, weak PFI-PE bands due to excitation of both even and odd quanta of the ν_2^+ and ν_3^+ modes are also observed in the PFI-PE spectra. The simulation of rotational contours resolved in PFI-PE vibronic bands associated with excitation to the (ν_1^+=0-1, ν_2^+=0-2, ν_3^+=0)$X^2\Pi_{3/2,1/2g}$, (ν_1^+=0-5, 0, 0)$A^2\Pi_{3/2,1/2u}$, (0,0,0)$B^2\Sigma_u^+$, and (0,0,0)$C^2\Sigma_g^+$ vibrational levels has yielded accurate ionization energies for the formation of these vibronic states from CO_2($X^1\Sigma_g^+$).

Adiabatic three dimensional potential energy functions (PEFs) for CO_2^+($B^2\Sigma_u^+$ and $C^2\Sigma_g^+$) have also been generated theoretically using the complete active space self-consistent field and internally contracted multi-reference configuration interaction methods. Based on these PEFs, vibronic energy levels for CO_2^+($B^2\Sigma_u^+$ and $C^2\Sigma_g^+$), together with their Franck-Condon factors, are calculated for comparison with PFI-PE bands resolved in the experimental spectra. This comparison has identified PFI-PE bands for CO_2^+($B^2\Sigma_u^+$ and $C^2\Sigma_g^+$) due to anharmonic resonance and several members of Fermi polyads. The analysis of PFI-PE spectra also reveals the threshold for dissociation of CO_2 to CO($X^1\Sigma^+$) + O^+(^4S) at 19.0697eV, and the threshold for dissociation of CO_2 to CO^+($X^2\Sigma^+$) + O($^3P_2$) at 19.4683eV.

EXPERIMENT

The experiments were carried out at the Chemical Dynamics Beamline of the ALS. The beamline consists of a 10-cm period undulator, a gas harmonic filter, a 6.65 m off-plane Eagle mounted monochromator, and a multi-purpose photoelectron-photoion spectrometer, all of which have been described in previous publications.[1-3] In the experiment, helium was used in the harmonic gas filter to suppress the higher undulator harmonics with photon energies greater than 24.59 eV. Undulator light of the first harmonic emerging from the gas filter was directed into the monochromator and dispersed by a 4800 lines/mm grating (dispersion = 0.32 /mm) before entering the photoelectron-photoion apparatus. The monochromator entrance/exit slits used were in the range of 25/25-300/300 μm, corresponding to the nominal wavelength resolution range of 0.008-0.096 Å (FWHM).

The CO_2 sample was introduced into the photoionization-photoexcitation (PI/PEX) region as a continuous, neat CO_2 molecular beam by supersonic expansion from a room temperature stainless steel nozzle at a stagnation pressure of 760 Torr, the rotational temperature of CO_2 beam is around 200K. The procedure used for the present multibunch synchrotron-based PFI-PE measurements has been described in details previously. [3] Briefly, the ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns. In each storage ring period, there is a 16-ns dark gap consisting of 8 consecutive unfilled buckets for the ejection of cations from the ring orbit. A nominally zero electrostatic dc field was maintained across the PI/PEX region prior to the application of a pulsed electric field (height = 0.54 V/cm, width = 42 ns) to the repeller plates for PFI. The pulsed electric field was centered at the 16-ns dark gap of the synchrotron ring period. In the present experiment, the pulsed electrical field was applied every other synchrotron ring periods, i.e., 1.312 μs, corresponding to a repetition rate of 0.76 MHz.

The intensity for the monochromatized VUV beam was monitored by a tungsten photoelectric detector. Spectra were flux normalized by the corresponding VUV photon intensities. The energy step sizes used were in the range of 0.2-0.5 meV and the counting times for each step varied in the range of 2-5 seconds. All PFI-PE spectra were calibrated before and after each measurement using the $Ar^+(^2P_{3/2})$ and $Ne^+(^2P_{3/2})$ PFI-PE bands obtained under the same experimental conditions. This calibration scheme assumes that the Stark shifts of the IEs of CO_2 and rare gases are identical. Previous measurements indicate that the accuracy of this calibration method is within ±0.5 meV.

RESULTS AND DISCUSSION

A. Ionization energies and vibrational frequencies for $CO_2^+(X^2P_g, A^2P_u, B^2S_u^+$ or $C^2S_g^+)$

The dominant electronic configuration of the neutral $CO_2(X^1\Sigma_g^+)$ ground state is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$. Removing an electron from the $1\pi_g$, $1\pi_u$, $3\sigma_u$, or $4\sigma_g$ orbital gives $CO_2^+(X^2\Pi_g, A^2\Pi_u, B^2\Sigma_u^+$ or $C^2\Sigma_g^+)$ state, respectively. Fig.1 shows the PFI-PE spectrum for $CO_2^+(X^2\Pi_g, A^2\Pi_u, B^2\Sigma_u^+$ and $C^2\Sigma_g^+)$ in the full energy range of 13.6-20.0eV. The adiabatic ionization energies based on BOS simulation and vibrational frequencies for $CO_2^+(X^2\Pi_g, A^2\Pi_u, B^2\Sigma_u^+$ and $C^2\Sigma_g^+)$ states are summarized in Table I, together with the ab initio calculation results.

Table I Adiabatic ionization energies and vibrational frequency values for CO_2^+

State		IE (cm^{-1})	$\nu_1^+(cm^{-1})$	$\nu_2^+(cm^{-1})$	$\nu_3^+(cm^{-1})$
$X^2\Pi_g$	PFI-PE	111115 ± 4	1239	516	1433
$A^2\Pi_u$	PFI-PE	139646 ± 4	1129	452	2623
$B^2\Sigma_u^+$	PFI-PE	145793 ± 4	1284	579	1891
	Ab initio	-	1291.6	603.0	1889.9
$C^2\Sigma_g^+$	PFI-PE	156396 ± 4	1390	626	2942
	Ab initio	-	1392.1	642.8	2993.9

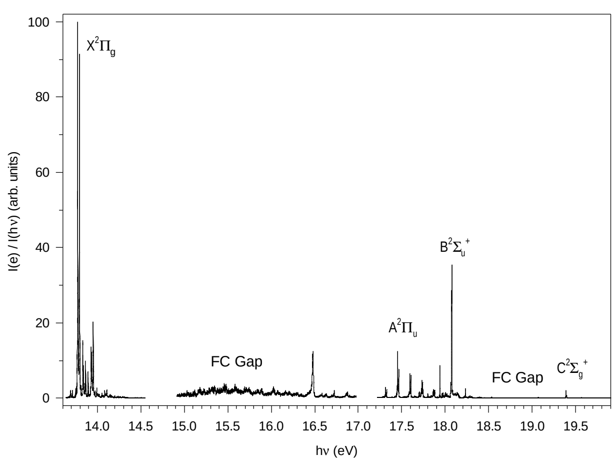

Fig.1 PFI-PE Spectrum for $CO_2^+(X^2\Pi_g, A^2\Pi_u, B^2\Sigma_u^+$ and $C^2\Sigma_g^+)$ in the full energy range of 13.6-20.0eV obtained with a PFI-PE resolution of 7 cm^{-1} (FWHM).

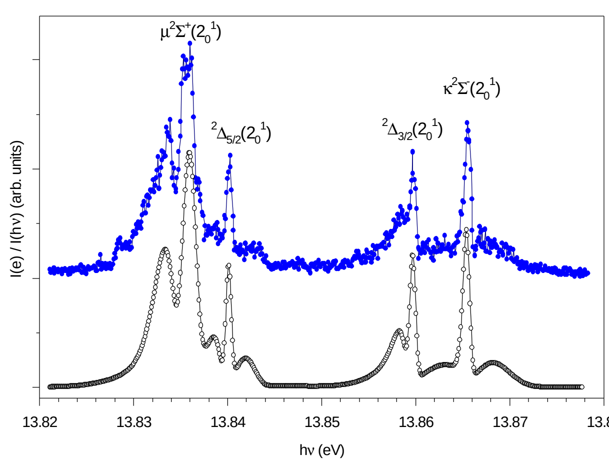

Fig. 2 Comparison of high-resolution PFI-PE spectra (•) and BOS simulated spectra (o) for $\mu^2\Sigma^+(2_0^1)$, $^2\Delta_{5/2}(2_0^1)$, $^2\Delta_{3/2}(2_0^1)$, and $\kappa^2\Sigma^-(2_0^1)$ in the energy range of 13.82-13.88eV, PFI-PE resolution = 4-5 cm^{-1} (FWHM).

B. Renner-Teller states associated with (0,1,0)$X^2\Pi_g$

The Renner-Teller structures due to the excitation of the ν_2^+ mode of CO_2^+ are of great interest to spectroscopic and theoretical studies. As a linear triatomic molecules with excitation of ν_2^+ quanta, the vibrational angular momentum along the molecular axis can have $l_v h/2p$, where $l_v = \nu_2^+, \nu_2^+ - 2, \ldots, 0$, or 1. Since the electronic orbital angular momentum has a nonzero projection of $Lh/2p$ along the molecular axis, the Renner-Teller coupling between Λ and l_v results in a new quantum number K=$|L \pm l_v|$ Including the Renner-Teller and spin-orbit couplings, the vibrational level (0,1,0)$X^2\Pi_g$ splits into four components $\mu^2\Sigma^+(2_0^1)$, $^2\Delta_{5/2}(2_0^1)$, $^2\Delta_{3/2}(2_0^1)$, and $\kappa^2\Sigma^-(2_0^1)$.

To obtain an accurate determination of the IEs for these four Renner-Teller levels, we have performed the BOS simulation for the experimental spectra (solid circles) shown in Figs. 2. The IEs determined from simulation are 13.8345, 13.8399, 13.8595 and 13.8656 eV for $\mu^2\Sigma^+(2_0^1)$, $^2\Delta_{5/2}(2_0^1)$, $^2\Delta_{3/2}(2_0^1)$, and $\kappa^2\Sigma^-(2_0^1)$, respectively. The energy expression for these states can be expressed as follows, where G values are energies with respect to $^2\Pi_{3/2g}(0_0^0)$, ν_2^+ are bending frequency, ε and g_k are Renner-Teller parameters, and r = ½[G($\kappa^2\Sigma^-(2_0^1)$) - G[$\mu^2\Sigma^+(2_0^1$

$$G[^2\Delta_{3/2}(2_0^1)] - \frac{1}{2}\{G[^2\Pi_{3/2}(0_0^0)] + G[^2\Pi_{1/2}(0_0^0)]\} = n_2^+ + g_k - \frac{1}{2}e^2 n_2^+ - \frac{1}{2}A(^2\Delta) \quad (1)$$

$$G[^2\Delta_{5/2}(2_0^1)] - \frac{1}{2}\{G[^2\Pi_{3/2}(0_0^0)] + G[^2\Pi_{1/2}(0_0^0)]\} = n_2^+ + g_k - \frac{1}{2}e^2 n_2^+ + \frac{1}{2}A(^2\Delta) \quad (2)$$

$$G[k^2\Sigma^-(2_0^1)] - \frac{1}{2}\{G[^2\Pi_{3/2}(0_0^0)] + G[^2\Pi_{1/2}(0_0^0)]\} = n_2^+ + r - g_k \quad (3)$$

$$G[m^2\Sigma^+(2_0^1)] - \frac{1}{2}\{G[^2\Pi_{3/2}(0_0^0)] + G[^2\Pi_{1/2}(0_0^0)]\} = n_2^+ - r - g_k \quad (4)$$

$$G[k^2\Sigma^-(2_0^1)] - G[m^2\Sigma^+(2_0^1)] = [A^2(^2\Sigma) + 4(en_2^+)^2]^{1/2} \quad (5)$$

$$A(^2\Delta) = A(^2\Sigma)(1 - \frac{3}{4}e^2)/(1 - \frac{1}{4}e^2) \quad (6)$$

Using the experimental determined G values for these Renner-Teller states, we have determined $\nu_2^+ = 516.4 cm^{-1}$, $\varepsilon = -0.187$, $g_k = 2.74\ cm^{-1}$, and $A(^2\Sigma) = -160.8 cm^{-1}$. These values are in excellent agreement with those from VUV laser PFI-PE measurements. [4]

REFERENCE

1. C-W. Hsu, M. Evans, P. Heimann, K.-T. Lu, and C. Y. Ng, J. Chem. Phys. **105**, 3950 (1996).
2. P. Heimann, M. Koike, C-W Hsu, M. Evans, K. T. Lu, C. Y. Ng, A. Suits, and Y. T. Lee, Rev. Sci. Instrum. **68**, 1945 (1997).
3. C.-W. Hsu, M. Evans, C. Y. Ng, and P. Heimann, Rev. Sci. Instrum. **68**, 1694 (1997).
4. F. Merkt, S. R. Mackenzie, R. J. Rednall, and T. P. Softley, J. Chem. Phys. **99**, 8430 (1993).

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 for the Lawrence Berkeley National Laboratory and Contract No. W-7405-Eng-82 for the Ames Laboratory.

Principal investigator: Prof. C.Y. Ng, Ames Laboratory, USDOE and Department of Chemistry,
Iowa State University, Ames, IA 50011, USA. Email: cyng@ameslab.gov. Telephone: 515-294-4225