Journal of Electron Spectroscopy and Related Phenomena 79 (1996) 511–514

A high resolution study of the photelectron angular distributions and branching ratios for the carbon dioxide molecule in the wavelength region 685-795Å

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Measurements of the vibrational branching ratios and photoelectron angular distributions have been made in the regions of the Tanaka-Ogawa, Lindholm and Henning series for the CO_2 molecule. The behaviour of these parameters was found to be sensitive to which particular resonance is excited, with considerable intensity going into vibrational modes other than the symmetric stretch. An initial analysis of some of the data taken is presented.

1. INTRODUCTION

It has been known for some time that the photoionization spectrum of carbon dioxide contains prominent series of autoionizing resonances converging to the A $^2\Pi_u$ and B $^2\Sigma_u^+$ ionization limits. Although not all the structure has been identified, several vibrational and Rydberg progressions have been and are now known as the Tanaka-Ogawa (TO) series, the Lindholm (L) series and the Henning sharp(s) and diffuse(d) series. Using spectrographic methods, Tanaka and Ogawa[1] identified several Rydberg series converging onto the first eight vibrational levels of the A state, and each of these is split by spin-orbit coupling with the series converging onto the $^2\Pi_{1/2}$ limit being the stronger. A further progression seen by Tanaka et al[2] was later assigned by Lindholm[3] as a vibrational progression with principal quantum number 3. The other most prominent series were first seen by Henning[4] and converge to the ground vibrational level of the B state of the CO_2^+ ion.

A full consideration of the symmetries of the series was given recently by Parr et al[5]; in summary, in the case of the TO series some doubt remains but the balance of the experimental and theoretical evidence points to this having an $nd\delta_g$ configuration. The Henning sharp and diffuse series are now firmly believed to have $nd\sigma_g$ and $ns\sigma_g$ symmetries respectively.

The study presented here was undertaken to examine the response of angular distribution parameters and branching ratios to complex resonant structure in the photoionization spectrum, with improved electron spectrometer resolution and over a wide wavelength range.

2. EXPERIMENTAL PROCEDURE

This experiment was carried out on a 5 metre normal incidence monochromator fitted to a beamline at the Daresbury SRS, providing a photon flux of ~10^{10} photons/sec within a bandpass of 0.1Å. The light was brought into the experimental chamber by a 2mm diameter capillary light guide, which also served as a pressure differential between this chamber and the ultra high vacuum of the optical monochromator. The electron spectrometer[6] comprised two 100mm radius hemispherical analysers, one rotatable about the incoming light beam as axis and the other fixed. The fixed analyser accepted electrons ejected parallel to the E-vector of the incident radiation, and after calibration procedures were complete the rotatable analyser was set perpendicular to the E-vector. The polarization of the incoming light was measured using a three mirror polarizer with tungsten mesh and plate

0368-2048/96/$15.00
PII S0368-2048 (96) 02907-6

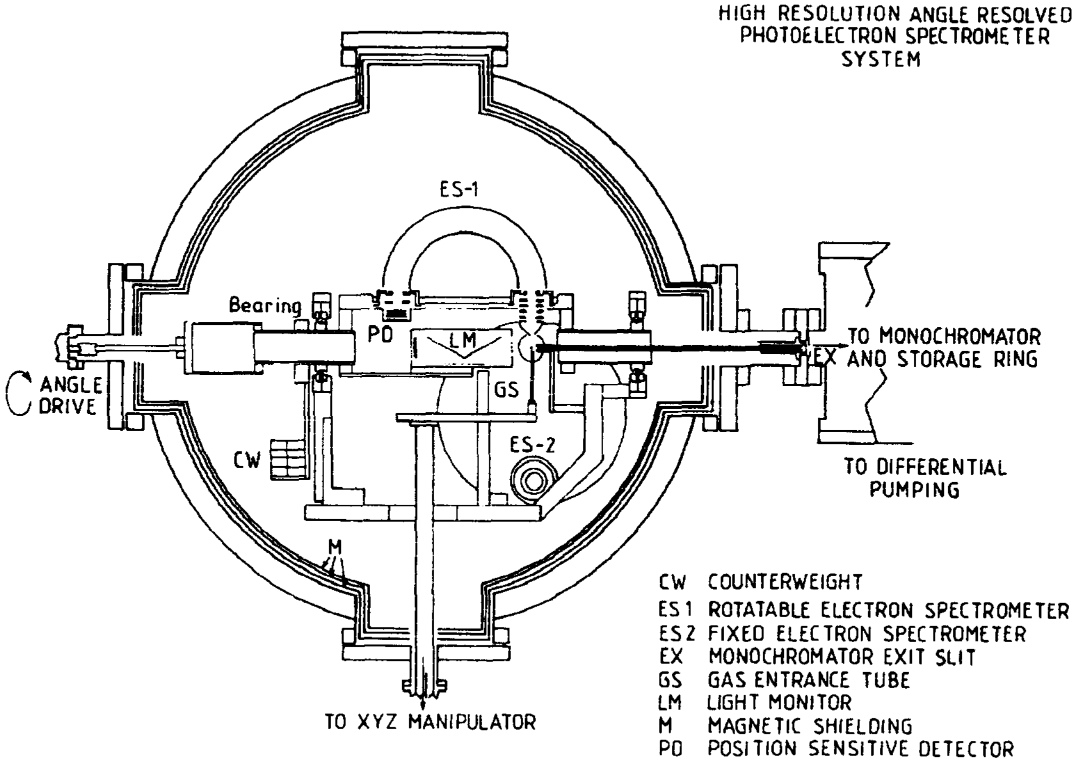

Figure 1 The experimental equipment used for the measurements

photodiodes which could be rotated with the rotatable analyser.

Calibration of the energy response of the analysers was done using argon or helium gas, using the known values of the cross section[7] and β-parameters[8]. Throughout the whole wavelength region studied here, measurements were taken at 0.1Å intervals, and the β-parameters and branching ratios calculated from the measurements made at the two angles using the well known expression

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left[1 + \frac{\beta}{4}(3p\cos 2\theta + 1)\right]$$

where θ is the angle between the major polarization axis and the ejected electron, p is the polarization of the incoming light, and σ is the partial cross section for the channel corresponding to the photoelectron being detected. In the case of this experiment, therefore, measurements were made simultaneously at $\theta = 0°$ and $\theta = 90°$. Altogether ~1500 data sets were taken in the wavelength region 650Å to 890Å. The data analysis was carried out by first correcting the raw data for the differing detection efficiencies of the two electron energy analysers. After normalization for detection efficiencies the data were fitted to a series of gaussian profiles using a least squares procedure, using as a basis the known levels of CO_2^+ identified by Chambaud et al[9]. The data were of sufficient quality to give reliable intensities for the vibrational components down to the 5% level.

3. RESULTS

With the large amount of data and the level of detail available to us, in this initial analysis we have concentrated on the response of the symmetric stretch vibrational members of the CO_2^+ ion to resonant structures. For the purposes of convenience and brevity, we have followed the notation adopted by McCulloh[10] to label the series members; for example $A5_2$ (TO) means the member of the Tanaka-Ogawa series for which the running number is 5 and the vibrational quantum number is 2. Bearing in mind that this series is now believed to have nd δ_g symmetry, the principal quantum number should be 4, ie one less than shown on the graphs. In the case of the Henning series, though using McCulloh's notation, we follow the reassignment given by Fridh et al[11], and the running numbers shown are the principal quantum numbers. This results in our labelling of the resonances being different from that in McCulloh's table.

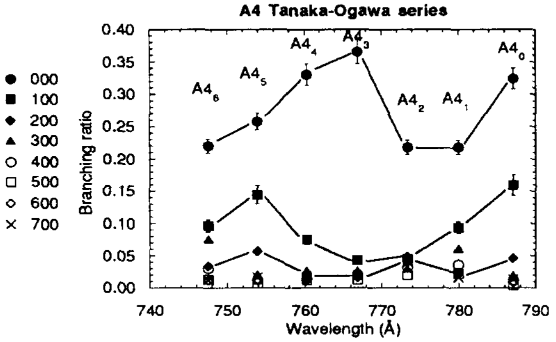

Figure 2. Branching ratios for the (000) vibrational members of CO_2^+ for the A4(TO) series.

We show in figure 2 the vibrational branching ratios for the first eight members of the symmetric stretch vibrational members in the CO_2^+ ion ground state, for the (TO) A_4 series of resonances. Although we can resolve the spin orbit split members of these series, the $^2\Pi_{1/2}$ components, at the shorter wavelength of the pair, have the larger intensities and are the ones to which we refer on the figures.

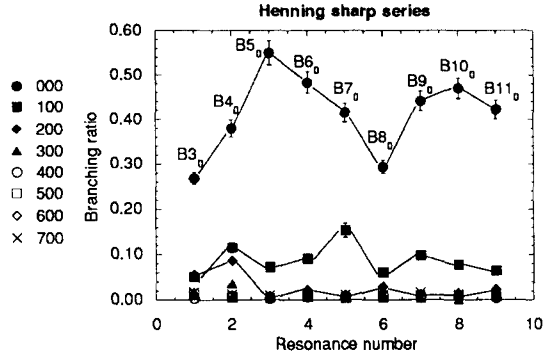

Figure 3. Branching ratios for the (000) vibrational members of CO_2^+ for the Henning sharp series. Note that in this figure the resonances have been numbered to avoid overcrowding on the diagram for the higher Rydberg members. The actual wavelengths are readily available from the literature; see, for example, reference 10.

The differing response of the CO_2^+ ion vibrational members to the resonances is obvious; although the (000) member always has the largest intensity the sum of the branching ratios at some resonances falls well below 0.5, indicating that a substantial intensity goes into the bending and anti-symmetric stretch vibrations. This is less true for the Henning series, for which the corresponding branching ratio data are shown in figure 3; in this case it can be seen that the (000) member tends to be larger, in comparison with the A4(TO) series.

With our experimental resolution of 40 meV, much of the weaker structure in the photoelectron spectrum is not resolved, nor is the spin-orbit splitting of the A $^2\Pi_u$ state. This limits us in the number of vibrational levels for which we can provide reliable angular distribution and branching ratio values, and is reflected in the error bars shown in the data, derived mainly from the quality of the least squares fit to the electron spectrum. However, in a separate experiment[5] using jet-cooled CO_2 and a spectrometer resolution of 17 meV, more structure was resolved. The results in figure 4 were taken at the peak of the A5$_2$, ie m = 5, (200) member of the TO series. This experiment was undertaken to show the selectivity in the autoionization of this state, and as can be seen it decays primarily to the $^2P_{1/2}$ level, consistent with the finding that the (TO) series converging to the $^2P_{1/2}$ limits are much more intense than those converging to the $^2P_{3/2}$ limits. From symmetry considerations[5] these data indicate that the (TO) series should be described by $\Omega_c\omega$ coupling. The known energy levels of members of the ($v_1$00), ($v_1$01) and ($v_1$02) progressions are shown as solid lines; the positions of the higher members were estimated by linear or quadratic extrapolation of the known levels. Also the Renner-Teller split (020) band is clearly seen.

The analysis and interpretation of these results is currently under way and will be the subject of a forthcoming publication.

4. ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Energy Research, under Contract

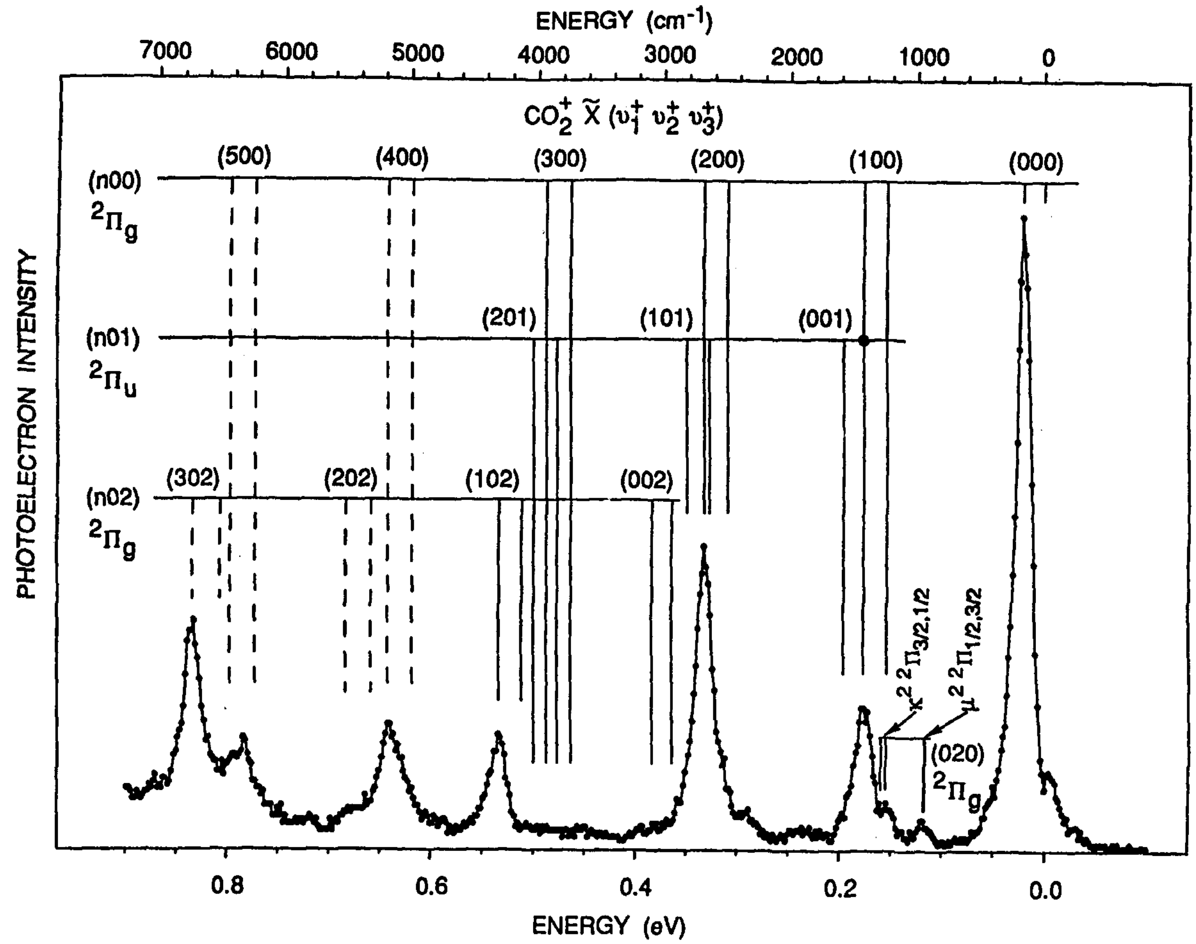

Figure 4. Photoelectron spectrum taken at the A5$_2$, m=5, (200) member of th (TO) series, at an analyser angle of 0°. The off-resonance contribution has been subtracted.

No. W-31-109-ENG-38 and by the Engineering and Physical Sciences Research Council, UK.

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