Photoionization of CO_2 and the Franck–Condon Principle for Polyatomic Molecules*

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Recent developments in the study of electrons produced in the photoionization of diatomic molecules have permitted comparison of calculated Franck–Condon factors with experimental determinations of relative vibronic-transition probabilities.[1-3] For the ionization of polyatomic molecules, however, the situation is different. In part this results from the greater difficulty in calculating Franck–Condon factors for complex systems.[4] This note reports measurements of threshold electrons produced in the photoionization of CO_2 and compares the results with previously calculated vibronic transition probabilities. The experimental method, which has been described,[3,5] confines attention to electrons produced at the thresholds corresponding to formation of distinct vibronic states. Briefly, photoelectrons produced by a dispersed photon beam are accelerated and then analyzed for this acceleration energy with a differential analyzer. Only the photon energy is varied while detecting electrons of the fixed acceleration energy. It is believed that the electron-detection efficiency remains constant under these conditions.

The spectrum obtained in CO_2 using 3-eV acceleration and analysis energy is shown in Fig. 1. We have plotted the measured ratio of electron-count rate to photon flux vs photon wavelength. The observed wavelength at the principal peak must be corrected for the instrument peak shift,[3,5] amounting to 1.2 Å. This yields an ionization potential at 899.9±0.5 Å in excellent agreement with the average wavelength of the accurately known doublet $^2\Pi_g \leftarrow {}^1\Sigma_g^-$ ionization potentials determined spectroscopically.[6] The instrument resolving power is insufficient to show the 0.020-eV doublet separation. However, two additional peaks, previously not resolved in photoelectron studies,[7] can be seen. The average peak spacing, 0.159±0.006 eV, coincides with the accurately known symmetric stretch frequency of the CO_2^+ molecule: $\nu_1 = 1280$ cm^{-1} (0.1587 eV).[8] Thus, the three peaks are attributed to the pro-

duction of ions in the vibrational levels 000, 100, and 200. Tanaka et al.[8] have reported a Rydberg series converging to the 100 level of the ion but did not find a series converging to the 200 level. Both Cook et al.[9] and Nakata et al.[10] have measured the photoionization cross section, and their curves indicate structure at the photon energy corresponding to the 100 ion level
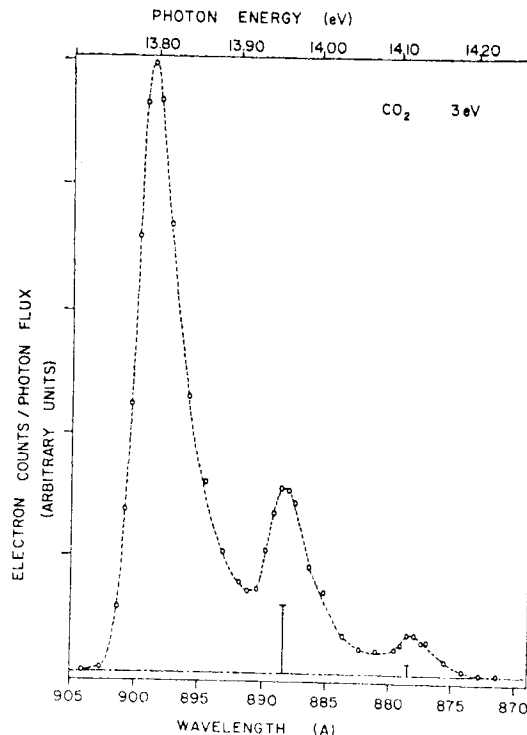

Fig. 1. Ratio of photoelectron count rate to photon flux as a function of the wavelength of the incident photon beam. Data for CO_2 using the indicated acceleration and analysis energy (see text). Pressure-independent background shown by horizontal dashed line, and calculated Franck–Condon factors, normalized to principal peak, shown by solid lines.

but not at the 200 level. Our results suggest that the very small probability for transition to the latter state is consistent with these observations.

Sharp and Rosenstock have calculated Franck–Condon factors in the harmonic approximation for the ionization of several linear symmetric molecules including carbon dioxide.[4] Their results, normalized to the amplitude of the principal peak, are shown as solid lines in Fig. 1. There is very good qualitative agreement between the results of this experiment and their calculations. However, even though the incomplete resolution of vibrational structure prevents an accurate experimental determination of the relative transition probabilities, our results suggest a quantitative discrepancy. It should be noted that the experimental method is sensitive to electrons produced by autoionizing excited states of the neutral molecule, provided that the initial kinetic energy of the released electron is smaller than the roughly 0.07-eV bandwidth of the electron energy analyzer. On the other hand, the ionization cross section[9,10] does not show structural features which may be interpreted as autoionization at these photon energies. Moreover, our results do not indicate structure due to autoionization. It is possible that the differences between the calculation and experiment may be due to neglect of anharmonicity.

We would also like to remark that the ion vibrational frequency ν_3 used in the calculations,[4] namely $\nu_3 = 2305$ cm^{-1}, is now regarded as resulting from incorrect assignment by Mrozowski. This was first recognized by Johns[11] who, in reinterpreting the data, presents a strong argument for $\nu_3 = 1469$ cm^{-1}. Using the general results of Sharp and Rosenstock this revised frequency yields a slightly altered set of Franck–Condon factors. The relative intensity of the transition to the 002 ion level as compared with the 000 level increases from 0.00012 to 0.028 when the smaller ν_3 frequency is used. The relative probability of exciting higher even harmonics of the ν_3 progression remains negligibly small. But the calculated relative intensities shown in Fig. 1 are unchanged. While the transition probability for the 002 level is thus expected to be comparable to that predicted for the 200 level, the data of Fig. 1 does not indicate a peak at the expected photon energy. Again, the influence of anharmonicity may alter the calculated value.

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