PHYSICAL REVIEW A VOLUME 23, NUMBER 6 JUNE 1981

Brief Reports

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Evidence for shape resonance in the $C\ ^2\Sigma_g^+$ band of CO_2^+ from angle-resolved photoelectron spectroscopy

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(Received 1 December 1980)

Angle-resolved photoelectron spectra were taken of the fourth band in CO_2 ($C\ ^2\Sigma_g^+$) as a function of photon energy using synchrotron radiation. It was found that the value of β dropped strongly in the vicinity of the photon energy of 42 eV. This result is shown to be in convincing agreement with theoretical predictions of a shape resonance, particularly when consideration is made of variations in internuclear distance.

I. INTRODUCTION

The multiple-scattering method has been demonstrated to be a highly effective means for calculating the photoelectric effect for molecules. One of its most interesting achievements lies in the prediction of shape resonances. These resonances arise from an electron excited into an electronic state from which it tunnels through a centrifugal molecular potential barrier into the continuum, and can be predicted within the framework of a single-electron model. Experimentally, shape resonances are seen as broad peaks in the cross-section curve. The identification of a shape resonance has been best carried out through the study of the partial cross sections of the individual molecular orbitals rather than by total cross sections. In addition, shape resonances strongly affect the angular distribution of the ejected photoelectrons.

Predictions of shape resonances were first made for diatomic molecules,[1-4] but similar effects have also been found for polyatomic molecules.[4] Shape resonances are expected both in the photoionization of valence[2-4] and core shell orbitals.[1,5,6] Experimentally, features in the partial photoelectron cross-section curves for the outermost orbital in both CO and N_2 were identified as shape resonances, but evaluation of the comparison was hampered by additional structure in the experimental curve.[7] The effects of a shape resonance on the angular parameter β for the ground vibrational state of these two cases were only modest and not ideal for an experimental assessment.[3,4] The effect of shape resonances on the excited vibrational states has been examined for the first photoionization band in CO and N_2 theoretically and experimentally for both branching ratios[8,9] and angular asymmetry parameters.[8,10,11] The agreement between experiment and theory is reasonable, but there remain many details unresolved.

Thus, the very strong shape resonance predicted[12] for the fourth band in the photoelectron spectrum of CO_2 was welcomed as an ideal test between theory and experiment. Unfortunately, the first examination with a continuous synchrotron radiation source of the cross section of the $4\sigma_g$ level in CO_2 led to negative results.[13] Subsequently, Brion and Tan,[14] using results on low-angle inelastic scattering, showed a very broad maximum in the optical strength that is probably caused by shape resonance. Calculations[4] on the $4\sigma_g$ orbital of CO_2 using the multiple-scattering method also predict an enormous dip in the value of the angular parameter β near 40 eV. With the help of synchrotron radiation we have measured β for the fourth band in the photoelectron spectrum of CO_2 and have unambiguously identified the shape resonance effect predicted by theory. Furthermore, we feel that this is one of the most convincing experimental verifications of shape resonance in the photoionization of molecules seen up to this time and should provide a benchmark for the comparison of theory and experiment.

II. EXPERIMENTAL

Angle-resolved photoelectron spectra were taken with an electron spectrometer and chamber designed for synchrotron radiation studies that will be described in detail elsewhere.[15] The angular asymmetry parameter β has been determined from relative intensities measured in the plane and perpendicular to the plane of polarization. The method of analysis is similar to that reported earlier.[11] The radiation was generated at the Synchrotron Radiation Center at Stoughton, Wisconsin. Data were taken from 584 to 475 Å with the aid of a one-meter Seya monochromator utilizing a grating blazed at 750 Å, and from 450 to 200 Å with help of a toroidal grating monochromator employing a three meter grating with a take off angle of 15° grazing incidence. For all the studies the resolution of the photon source was set at 2 Å and the resolution of the electron spectrometer at 80 mV.

III. RESULTS AND DISCUSSION

In Fig. 1 are plotted the angular asymmetry parameter β as determined from the angle-resolved photoelectron spectrum of the fourth band of CO_2 [specifically, the vibrational band corresponding to transitions to the final state $C\,^2\Sigma_g^+(v_{000})$]. The β values have been obtained experimentally from the relationship

$$\beta=\frac{4(R-1)}{3P(R+1)-(R-1)}\,.$$

R is $I(0°)/I(90°)$, where $I(0°)$ and $I(90°)$ are the intensities of photoelectrons moving in the direction parallel and perpendicular to the polarization vector. The polarization is treated as an experimentally determined variable and found from measurements on krypton[17] to be equivalent to approximately 80% over most of the energy range studied. The calculated values of β are also displayed in Fig. 1 and have been reported earlier[4] up to a photon energy of 45 eV. They have been extended to 60 eV in this paper. One change has been made in the calculations as reported previously. The value ω in Eq. (2) of Ref. 4 has been obtained from $\epsilon_f-\epsilon_i$ and not the experimental ionization potential. The calculations are based on the multiple-scattering method as adapted to photoionization cross sections. It is a single electron method, utilizing a statistically averaged potential for exchange and based on a fixed internuclear distance of 1.16 Å between the carbon and oxygen. (See Ref. 4 and references therein for details.)

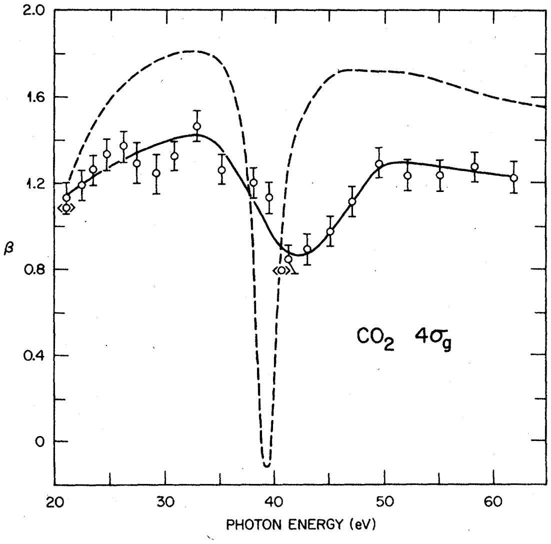

FIG. 1. Angular asymmetry parameter β obtained for the fourth band in the photoelectron spectrum of CO_2 representing the $C\,^2\Sigma_g^+$ state of CO_2^+ is plotted as a function of photon energy. Experimental data are given by open circles with error bars that reflect uncertainty in reproducibility. A solid line is given as an overall approximation to the experimental points. Besides the main dip seen at 42 eV, there may be an additional minimum in β near 29 eV, due to some process such as autoionization. The dashed line represents calculated values based on the multiple-scattering method using fixed internuclear distances. Values from the literature from line sources are given by ⟨○⟩ (see Ref. 16).

The calculations predict a very strong single dip in β with the minimum at a photon energy of 39.5 eV (the maximum range of β values that is physically possible is from +2 to −1). The experimental results clearly show this dip with a minimum slightly above theory at 42 eV. In addition, the experimental dip is broader and wider (about a factor of 3) than theoretical predictions. These differences between the calculations and experiment are not unreasonable and, in fact, are anticipated from the approximations employed in the theory. First, the nature of the shape resonance is strongly dependent on the internuclear distance. Thus, the results should be dependent on the vibrational motion of the molecule. Calculations which account for the effect of vibrational motion have been carried out by Swanson *et al.*[18] for the fourth band of CO_2, and their results show a broadening and reduction of the dip in β values that partly explain the results seen in Fig. 1. In addition, other effects may cause a dampening of the shape resonance. For example, it is well known in analogous resonances of atomic systems[19] that the use of a statistical exchange approximation will yield cross sections that can be considerably larger than those calculated with an exact treatment of exact treatment of exchange.

In conclusion, the experimental results on the β values for the fourth band of CO_2 plotted as a function of photon energy show a strong dip that is clearly the consequence of a shape resonance. These results give added confidence to the predictions of photoelectron cross sections of molecules that have utilized the multiple-scattering method. In addition, these experimental results should serve well as a benchmark or criteria against which future theoretical calculations can be evaluated.

ACKNOWLEDGMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corporation and by the University of Tennessee. The Synchrotron Radiation Center is operated under NSF Grant No. DMR-77-21888. Support at Wisconsin is currently from the Wisconsin Alumni Research Foundation.

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