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PREFACE

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FIGURE

ABSTRACT

Electron scattering spectra of CO_2 are reported in the 7- to 10-eV energy-loss range, at energies of 0.2, 0.35, 0.6, 0.7, and 7.0 eV above threshold, and at a scattering angle of 90 deg. Several new distinct overlapping continua with weak, diffuse bands superimposed are observed to lie in this energy-loss range. The experimental spectra are discussed in the light of recent ab initio configuration-interaction calculations of the vertical transition energies of CO_2. The experimental spectra are shown to be consistent with excitations to the $^3\Sigma_u^+$, $^{1,3}\Sigma_u^-$, $^{1,3}\Pi_g$, and $^{1,3}\Delta_u$ states of CO_2.

I. INTRODUCTION

Despite the great wealth of experimental knowledge available on carbon dioxide, not one single definitive assignment has yet been made of the features in the optical and electron scattering spectrum of CO_2 in the energy range 7 to 11 eV. The knowledge of both the location and symmetry of the electronic states (below 11 eV) is of great importance in interpreting the many processes (photon and low-energy electron scattering, dissociation, and recombination of CO(X) and O(^3P and ^1D)) that occur in planetary atmospheres and in the CO_2 gas laser. In this document we report the first detection of several low-lying electronic states of CO_2 lying between 7 and 10 eV above the ground state. These new excitations are observed along with peaks at 8.4 and 9.3 eV, which are seen both optically (Refs. 1 and 2) and in the electron scattering spectrum (Ref. 3) at higher impact energies (40 to 80 eV) and scattering angles near 0 deg. Extensive ab initio configuration-interaction calculations have recently been carried out of the vertical transition energies for excitation from the ground state to the low-lying (less than 12-eV) valence and Rydberg states of CO_2 (Ref. 4). With the aid of these calculations we are able to make assignments of the states giving rise to the newly-observed excitations.

II. INSTRUMENTATION

The apparatus used in the present measurements will also be described in some detail elsewhere (Ref. 5). Briefly, cylindrical analyzers are used in the electron impact spectrometer to energy-select both the incoming and scattered electron beams. A beam of low-energy electrons is focused onto a beam of molecules from a hypodermic needle source and scattered electrons are observed in the angular range $0° \leq \theta \leq 135$ deg. To obtain information on excitation processes near threshold, the instrument is operated in a constant residual-energy mode. That is, the incident electron energy E_0 and the energy-loss ΔE are swept linearly. Only those scattered electrons that are left with a fixed residual energy E_R such that $E_R = E_0 - \Delta E$ are detected by the electron analyzer. These electrons are counted, and the counts stored in a multichannel scalar as a function of ΔE.

III. RESULTS

In Fig. 1 we present energy-loss spectra at residual energies of 0.2, 0.35, 0.6, 0.7, and 7.0 eV. Spectra were obtained over a range of scattering angles, but for the sake of presentation we have shown in Fig. 1 only spectra obtained at 90 deg. The energy calibration of these spectra was made experimentally against the elastic peak ($\Delta E = 0$ eV), and confirmed by the location of a sharp feature at 11.40 eV (now shown in Fig. 1). Also shown for comparison (Fig. 1, top curve) is the optical absorption spectrum from Ref. 1. Since this last spectrum was reported on a wavelength, rather than energy scale, an accurate superposition with the electron scattering spectra is possible only near energies of 8.0 and 9.3 eV. We show also in Fig. 1 the results of ab initio configuration-interaction calculations (Ref. 4) of the excitation energies of CO_2. These energies were calculated at the linear CO_2 ground-state geometry, using the experimental O-C-O bond length.

As may be seen from the experimental spectra, the various electronic transitions in this 7- to 10-eV energy region overlap one another. We can, however, by a suitable choice of E_R and θ favor certain excitations (spin or symmetry-forbidden ones, for example) over others. To unravel the many features in the spectra (at least qualitatively at present) we proceed as follows. The location of the optical peaks at 8.4 and 9.3 eV correspond to the $^1\Delta_u \cdot \tilde{X}$ and $^1\Pi_g \cdot \tilde{X}$ transitions calculated to lie at 8.38 and 9.23 eV, respectively (Ref. 4). We would expect the optical spectrum to resemble most closely the electron scattering spectrum taken at a large residual energy. Thus, the peak observed in the $E_R = 7.0$-eV spectrum at ~ 8.6 eV, and the weaker shoulder at ~ 9.4 eV are primarily due to the $^1\Delta_u \cdot \tilde{X}$ and $^1\Pi_g \cdot \tilde{X}$ transitions, respectively. The transitions to the $^3\Delta_u$ and $^3\Pi_g$ states are calculated to lie at 7.83 and 8.95 eV, respectively

(Ref. 4), and are thus well separated from the other transitions. Since the transitions to these states are both spin and symmetry-forbidden, we expect that their clearest indication will be in the spectra obtained close to threshold. Two fairly well-isolated peaks are observed at ~ 8.1 and ~ 8.8 eV in the spectrum at $E_R = 0.6$ eV. These excitations are very likely composed primarily of the $^3\Delta_u \leftarrow \tilde{X}$ and $^3\Pi_g \leftarrow \tilde{X}$ transitions, respectively. Further, we note that the excitation to these two states appears to weaken abruptly between $E_R = 0.35$ eV and $E_R = 0.2$ eV. At $E_R = 0.2$ eV there appears only a single peak at ~ 8.3 eV, with a smaller shoulder at ~ 9.3 eV. The region of the main peak corresponds to the location of the $^1\Sigma_u^-$, $^3\Sigma_u^-$, and $^1\Delta_u$ states. Since the vibronically-allowed $^1\Delta_u \leftarrow \tilde{X}$ transition is already weak at $E_R = 0.6$ eV relative to the spin and symmetry-forbidden transitions, we expect it to be very nearly absent in the $E_R = 0.2$-eV spectrum. The main peak at ~ 8.3 eV therefore must be primarily due to either or both the spin and symmetry-forbidden $^3\Sigma_u^- \leftarrow \tilde{X}$ and symmetry-forbidden $^1\Sigma_u^- \leftarrow \tilde{X}$ transitions calculated to lie at 8.24 and 8.27 eV, respectively (Ref. 4). These transitions would be $^{1,3}A_2 \leftarrow \tilde{X}\ ^1A_1$ in C_{2v} symmetry, so that their degree of forbiddenness would be unchanged upon bending of the CO_2 molecule. This assignment is also confirmed by the fact that in a spectrum (not shown) taken at the same residual energy, $E_R = 0.2$ eV, but at 20 deg the 8.3-eV peak becomes very weak. This behavior is typical of $\Sigma^- \leftarrow \Sigma^+$ transitions (Ref. 6). The broad shoulder at ~9.3 eV is very likely a weak contribution from the $^1\Pi_g \leftarrow \tilde{X}$ transition.

The $^3\Sigma_u^+ \leftarrow \tilde{X}$ transition is calculated to lie at 7.35 eV, and appears to be present only weakly in the spectra. It may be present as the slight break in slope on the low-energy edge of the $E_R = 7.0$-eV spectrum, and is probably obscured by the next $^3\Delta_u \leftarrow \tilde{X}$ transition in the spectra at $E_R = 0.7$, 0.6, and 0.35 eV. A more complete deconvolution of our spectra taken at several scattering angles and residual energies will be helpful in giving the relative contribution of this $^3\Sigma_u^+ \leftarrow \tilde{X}$ transition, as well as of the remaining transitions, to the overall spectra. Such a deconvolution may not be unique but will provide limits to the relative contributions of each transition. This work is now in progress.

The vibrational bands superimposed on the broad peaks have energy locations and spacings that vary from one spectrum to another. These bands thus do not belong to a single progression, but to progressions in several electronic states. Also, the banded structure in these spectra (as well as in spectra of other polyatomic molecules) may arise in several ways. First, a particular upper state may be bound in all vibrational coordinates. For example, the ${}^3\Sigma_u^+$, ${}^3\Delta_u$, and ${}^1\Sigma_u^-$ states must correlate at large OC-O distances, and, in the linear geometry, to first states of CO + O, which can give rise to these state symmetries of CO_2. The dissociation limit of proper symmetry is into $CO(a\,{}^3\Pi) + O({}^3P)$ at 11.55 eV. We would thus expect the ${}^3\Sigma_u^+$, ${}^3\Delta_u$, and ${}^1\Sigma_u^-$ states to be bound in the ν_1, ν_2, and ν_3 vibrations, and to give rise to banded structure in the spectra. This argument would be complicated by predissociation of these bound states upon bending of the molecule. This predissociation would arise by mixing of the bent ${}^{1,3}A_2$ and ${}^{1,3}B_2$ components of these bound states with like components of the nearby ${}^3\Sigma_u^-$, ${}^3\Pi_g$, and ${}^1\Delta_u$ states correlating to lower dissociation limits. Second, a particular upper state may be repulsive in nature, dissociating into some states of CO + O. However, the molecule may execute several oscillations in the ν_3 mode before dissociating. Such a Lissajous motion (Ref. 7) in the excited state could give rise to diffuse bands, even though the excitation is into a region that would be a continuum in the case of a diatomic molecule. Considering these two effects, it is difficult to infer from the appearance of bands in our spectra that such bands imply a truly bound upper state, rather than a repulsive state in which several ν_3 oscillations prior to dissociation are possible.

IV. CONCLUSIONS

The observation of electron-impact spectra in the threshold region with varying residual energies and scattering angles has shown itself to be a particularly powerful tool in revealing the excited states of CO_2. In the course of this work special attention was paid to the possible presence of electronic states in the Franck-Condon region below 7 eV. No such energy-loss processes were observed, and it is felt that if they were present, this experimental technique would have detected them. Further study of the energy and angular behavior of these new low-lying states will be reported later.

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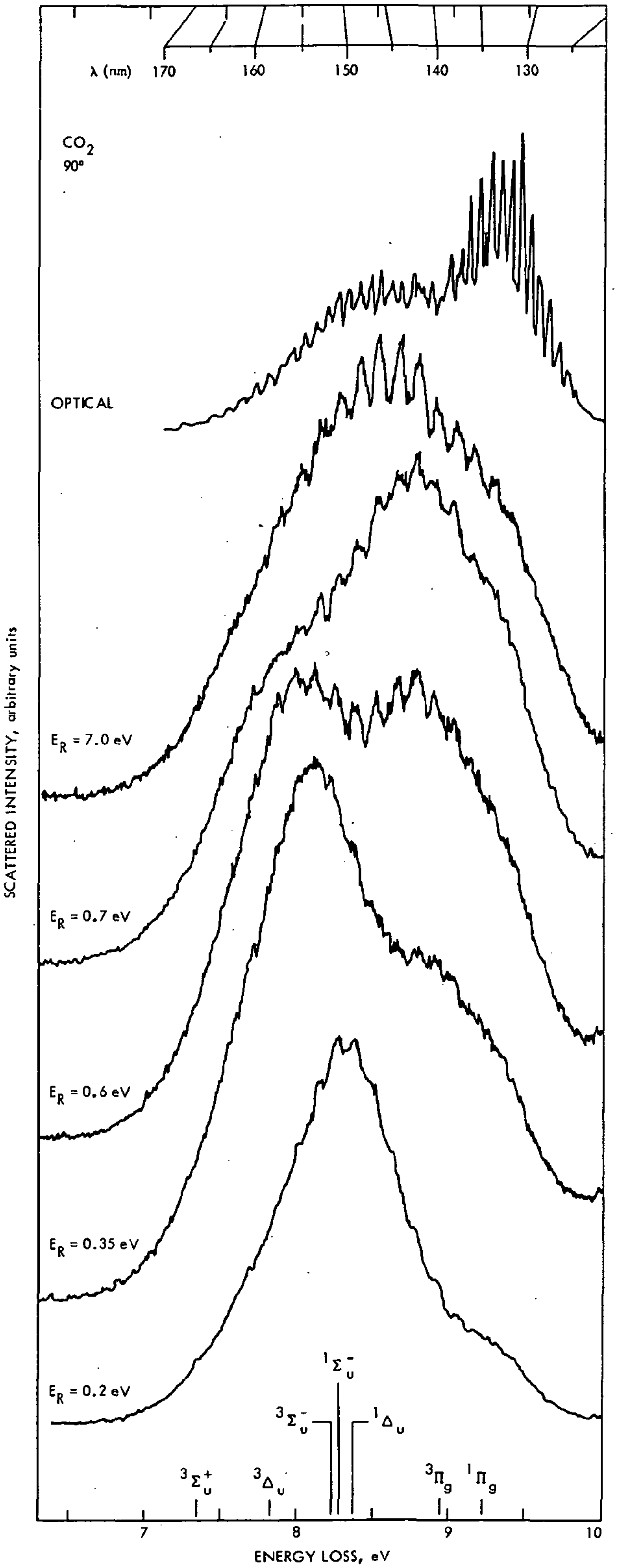

Fig. 1. Energy-loss spectra of CO_2 at 90° scattering angle in the energy-loss range 7 to 10 eV.

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