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Double *e*-beam technique for collision studies from excited states: Application to vibrationally excited CO_2

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We describe a new technique which utilizes two beams of electrons to study the electron scattering from the excited states of atoms and molecules. The capability of the technique is specifically demonstrated by applying it to the process of dissociative electron attachment with vibrationally excited CO_2.

Electron scattering from the excited states of atoms and molecules plays an important role in high-temperature plasmas, gas dischanges, and auroras. However, the cross sections for this process are not known accurately, principally because it is difficult to produce a sufficiently high number density of excited-state species to enable the collision studies. In the past, tunable lasers have been employed for excitation but for various reasons only a limited number of species could be investigated in this manner.

We present here a technique which utilizes two beams of electrons for studying the scattering of electrons from excited states. A schematic diagram illustrating the principle of the technique is shown in Fig. 1. It employs a crossed electron beam-target beam geometry. The target beam is produced by flowing the gas under study through a capillary array or a hypodermic needle. This beam is crossed at 90° by two beams of electrons traveling in opposite directions. The electron energies of the two beams can be varied independently. Each of the electron beams is collimated by a magnetic field (B field) produced by a solenoid. One beam (beam No. 2) is used to excite the target species to its various excited states, and the other beam (beam No. 1) is utilized to observe the scattering from the excited states. These beams of electrons are energy unselected. Their energy profiles were obtained by utilizing the retarding potential on a Faraday cup. It was found that the full width at half maximum (FWHM) of individual beams was approximately 300 meV. The energy of the electrons is varied by changing the bias on the filament with respect to the last electrode of each electron gun. This electrode is kept at ground (earth) potential. The beam current, as measured by a Faraday cup in a separate experiment, remained constant as the energy of the beam was changed from 0.5 to about 20 eV, which is the energy range of the present interest. Although the energy of the electron beam can be obtained by recording the filament bias voltage, the contact potentials at various surfaces tend to change it from its actual value. In the present work the energy of the beams was calibrated by utilizing the previously well-known peak values of electron attachment energies for H^--H_2, O^--O_2, and O^--CO_2. It was found that the filament bias voltage needed a correction of +0.5 V to get the true energy of the electron beam. We estimate that after correction the energy of the individual electron beams is accurate to within 0.1 eV. In general, the current in the e beam No. 1

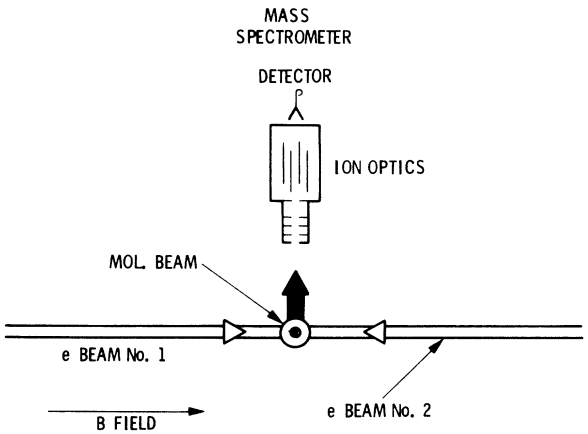

FIG. 1. Conceptual diagram of the double *e*-beam arrangement.

was 3.6×10^{-6} A and in the e beam No. 2 it was 0.1×10^{-3} A. A detailed description of the apparatus is given in Ref. 1. A vacuum of about 10^{-8} Torr was obtained when the gas forming the molecular beam was not flowed into the vacuum chamber. However, the pressure rose to about 10^{-7} Torr when the molecular beam was on. Under these conditions the pressure in the molecular beam is estimated to be less than about 10^{-3} Torr. At this pressure the probability of multiple scattering is negligible.

This technique is quite suitable for studying the process of dissociative electron attachment with rotationally vibrationally excited states of molecules. The cross sections for this process are expected to be quite large. In the past, the rotationally and vibrationally excited states were produced by heating[2–4] the gas under study in a crucible. However, due to practical limitations imposed by high temperatures, only low-lying vibrational states were generated. On the other hand, by utilizing a beam of electrons higher vibrational states and even electronic states of the molecules can be populated.

We present here the application of the above technique to the study of dissociative attachment with vibrationally excited states of CO_2. In dissociative attachment the following reaction takes place:

$$e + CO_2 \rightarrow CO_2^- \rightarrow CO + O^- \quad . \tag{1}$$

The 0^- ions are produced for certain specific energies of electrons. These ions are extracted out of the interaction region by an electric field of the order of 2 to 3 V/cm applied at 90° to both the electron beam and molecular beam. The ions are then focused at the entrance aperture of a quadrupole mass spectrometer by ion lenses.

The mass spectrometer was set to detect O^-. The procedure for obtaining the resonance energies and relative values of cross sections was as follows. First, the electron beam No. 2 (Fig. 1) was turned off. Then the electron energy of the beam No. 1 was varied. The output signal from the mass spectrometer was recorded by a multichannel scalar as a function of electron energy. An example of the variation of the O^- signal as a function of electron energy thus obtained is shown in Fig. 2(a). In the energy region of 0 to 20 eV, six intensity peaks were seen. These lay at 4.4 ±0.1, 8.2 ±0.1, 13.0 ±0.2, 15 ±0.5, 16.9 ±0.2, and 19.4 ±0.2 eV, respectively. The first two were the most intense ones. In the second step, the electron beam No. 2 (Fig. 1) was also turned on. Its energy was fixed at 1.2 eV, based upon knowledge that at about this energy the vibrational excitation cross sections for CO_2 are largest[5] ($\simeq 10^{-16}$ cm^2). Thus the electron beam No. 2 populates the vibrationally excited states of CO_2. The energy of the electron beam No. 1 was again varied from 0 to 20 eV. The resulting spectrum is shown in Fig. 2(b). We found that the intensities of the spectral features

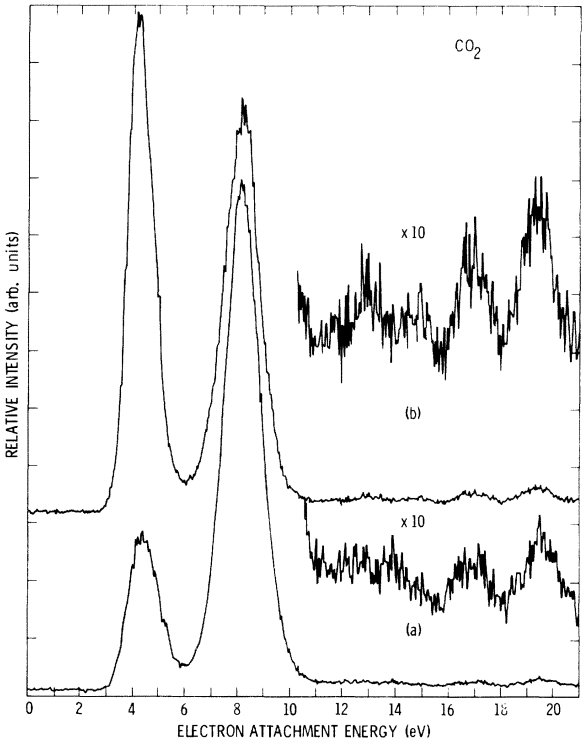

FIG. 2. (a) O^--CO_2 signal as a function of energy of e beam No. 1 and e beam No. 2 off. (b) O^--CO_2 signal as a function of energy of e beam No. 1 and e beam No. 2 fixed at 1.2 eV.

were enhanced and the intensity of the resonance peak at 4.4 eV was larger than that at 8.2 eV. This shows that the cross sections for the dissociative attachment at 4.4 eV increase when CO_2 is vibrationally excited. This observation was further supported by the increase in the O^- intensity when beam No. 1 (Fig. 1) was fixed at 4.4 eV and beam No. 2 was swept from 0 to 5 eV. The resulting spectrum is shown in Fig. 3. It is seen in this figure that when electron beam No. 2 has an energy of about 1.0 eV the O^- signal goes through a maximum. This is in agreement with Boness and Schulz[5] who found a maximum in the vibrational excitation at about 1.0 eV.

O^- production from CO_2 has been studied in the past by several researchers.[2,3,6] Mainly, these studies have been related to the measurement of cross sections (a) at room temperature, (b) at higher temperatures, and (c) the measurement of kinetic energy of O^- fragments. In general, the following conclusions have been drawn: (i) There are three peaks[3] for the O^- intensity at 4.4, 8.2, and 13.0 eV, respectively; (ii) the ratio of intensities of these peaks depends on the temperature[2] of CO_2, showing that the cross sections change with the vibrational population in the ground state. Furthermore, the thresholds for the formation of O^- are also temperature dependent,[2]

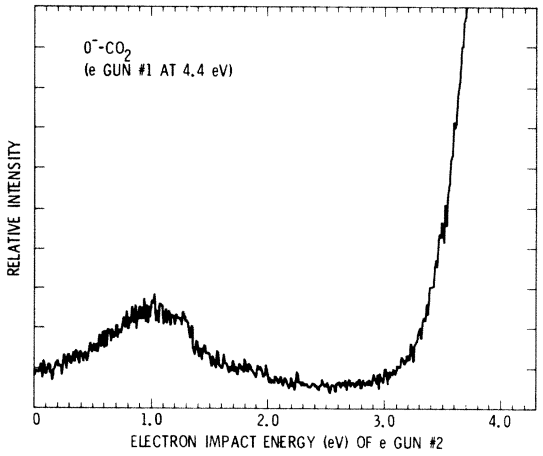

FIG. 3. O^--CO_2 signal with e beam No. 1 fixed at 4.2 eV and e beam No. 2 swept from 0 to 4 eV.

with shift toward lower energies as the temperature increases; and (iii) vibrationally excited CO is formed as a result of dissociation.[7]

The present work shows [Fig. 2(a)] that, in addition to the three O^- peaks observed before, there exist three additional peaks. The ratio of the intensity of the peak at 8.2 to that at 4.4 eV is 3.0 ± 0.1, which is in excellent agreement with previous measurements.[2] We also find that when CO_2 is excited by the e beam No. 2 the intensity of the 4.4-eV feature [Fig. 2(b)] increases to the extent that the ratio of the 4.4- to the 8.2-eV peak becomes greater than 1.0. This is also in agreement with the previous results. However, the present work does not show any appreciable increase in the intensity of other features, such as a shift[2] in the threshold value of the excitation or an increase in the intensity of the valley[3] between the 4.4- and 8.2-eV features. This is contrary to the previous findings[2,3] which were obtained for vibrationally excited CO_2 populated by heating in a high-temperature crucible. In our view the reason for this difference lies in the method of exciting the vibrational modes in CO_2. As shown by Boness and Schulz[5] by use of electron impact, principally the asymmetric stretch mode (001) is excited. However, by heating, all the vibrational and rotational modes are excited. The coupling of these states with the CO_2^- states may be different from the single asymmetric stretch mode generated by the electron impact.

In order to fully understand the process of dissociative attachment with CO_2 one needs to know details on the various potential-energy surfaces of CO_2^-. There are two previous calculations by Claydon *et al.*[8] (INDO SCF theory) and by England *et al.*[9] (*ab initio* SCF calculations). These calculations explain the onset of the 4.4-eV feature very well and assign a $^2\Pi_u$ state of CO_2^- to be responsible for the O^- production. However, $^2\Sigma_g^+$ state shape resonance, as calculated by Claydon *et al.*, does not accurately account for the threshold or the peak position of the 8.2-eV feature (Fig. 2). A similar situation exists with the higher-energy peaks. Our results showing small dependence of cross sections on vibrational excitation indicate that the 8.2-eV feature and the features at higher energies originate from CO_2^- states which are Feshbach resonances, rather than shape resonances. Because the vibrational excitation strongly affects the shape resonances (potential scattering), the dramatic change in the intensity of the 4.4-eV feature ($^2\Pi_u$ CO_2^- state) takes place. However, the 8.2-eV and higher-energy features result from electronic rearrangement in the molecule (Feshbach resonances) and do not depend appreciably upon nuclear motion. Winter[10] has carried out Hartree-Fock calculations with large basis sets for some of these higher CO_2^- states. These calculations predict a $^2\Pi_g$ Feshbach resonance at 8.3 eV. This state has an electronic configuration of

$$1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 4\sigma_g^2 1\sigma_u^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 1\pi_g^3 3s\sigma_g^2\,{}^2\Pi_g \ .$$

Its parent states are $1,3\pi_g$ whose energies are 9.0 and 9.3 eV for the triplet and singlet states, respectively.

In conclusion, we find that the double e-beam technique can be successfully employed for studying the electron scattering from excited states. It has been demonstrated clearly, using CO_2 as an example, that upon selecting proper energies the various vibrational states can be excited, from which the process of dissociative attachment can be studied. This technique may find wide application for certain special types of measurements, and is of immediate interest in this regard.

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