PHYSICAL REVIEW
LETTERS

VOLUME 21 7 OCTOBER 1968 NUMBER 15

VIBRATIONAL EXCITATION OF CO_2 BY ELECTRON IMPACT*

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(Received 2 August 1968)

Vibrational excitation of CO_2 is studied using a double electrostatic analyzer. The asymmetric stretch vibration (001) exhibits a peak cross section about 3×10^{-16} cm^2 at 0.9 eV, and the 002 mode excitation is an order of magnitude lower. Six energy loss peaks associated with the symmetric stretch mode (100, 200, etc.) are observed in the energy range 3-4.5 eV, with a peak at 3.8 eV. The data are consistent with the existence of two short-lived compound states. The first, around 0.9 eV, exhibits *p*-wave character, and the second, around 3.8 eV, exhibits *s*-wave behavior.

Vibrational excitation of diatomic molecules has been the subject of extensive experimental[1-5] and theoretical[6-8] investigations in the past few years, and the experimentally observed structures, as well as the magnitude of the cross sections, can be successfully understood by considering the existence of compound states. It is desirable to test the validity of the model applicable for diatomic molecules for the case of more complex molecules. This Letter reports results for a linear triatomic molecule, and we find the model of the compound state very useful in interpreting our results. We chose CO_2 as the subject of these initial experiments because of the current interest in CO_2 as a laser medium and because of the geometrical symmetry and simplicity of the molecule.

A double electrostatic analyzer,[1] similar to that described previously, has been used for this study. The first electrostatic analyzer forms an electron beam with a half-width about 0.06 eV. The electrons are accelerated into the collision chamber where they are crossed by a beam of CO_2 molecules. Those electrons which lose energy in exciting vibrational levels in CO_2 and are scattered into the acceptance angle of the second analyzer are transmitted to a "channeltron" electron multiplier, and measured on an electrometer. The two electrostatic analyzers can be rotated with respect to each other for measurements of angular dependences.

The experiment consists of measuring the energy-loss spectrum at various fixed incident electron energies at 45, 72, and 90 deg. This is accomplished by sweeping the voltage between the first and second electrostatic analyzer while keeping the electron energy in the collision region fixed. Peaks in the curves thus obtained are associated with energy-loss processes to the CO_2 molecule. Figure 1 shows examples of the curves obtained at electron energies of 1.4 and 3.8 eV.

The two energy-loss spectra shown in Fig. 1 have different characteristics. The energy-loss spectrum shown at the top of Fig. 1 is typical for incident electron energies in the range 0.3-3 eV, and the energy-loss spectrum shown in the lower portion of Fig. 1 is characteristic for the range 3-4.5 eV. In the low-energy regime the predominant features are energy-loss peaks at 0.29 and 0.58 eV. Energy losses smaller than 0.29 eV are indicated by unresolved structure. In the

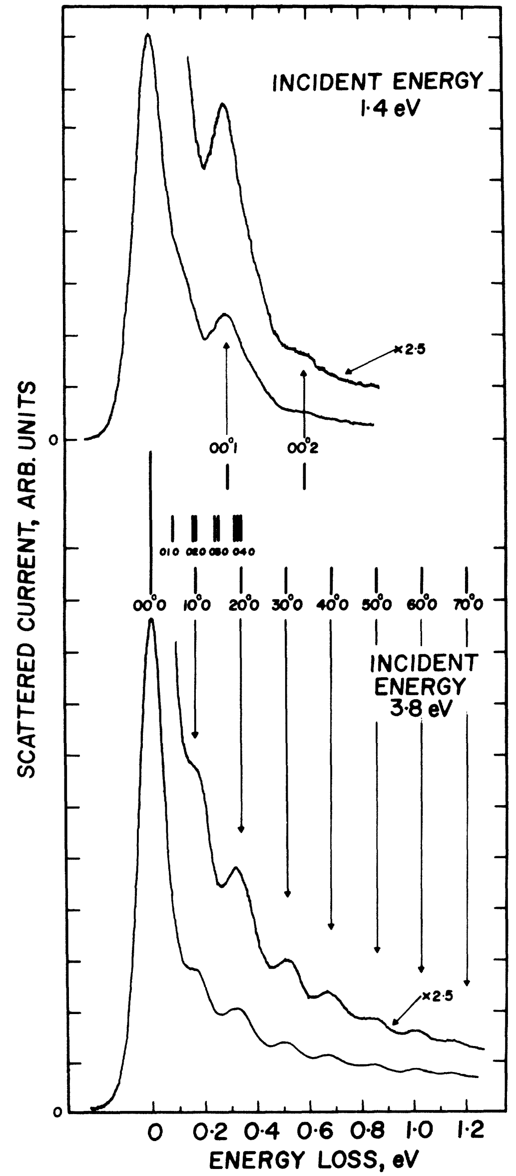
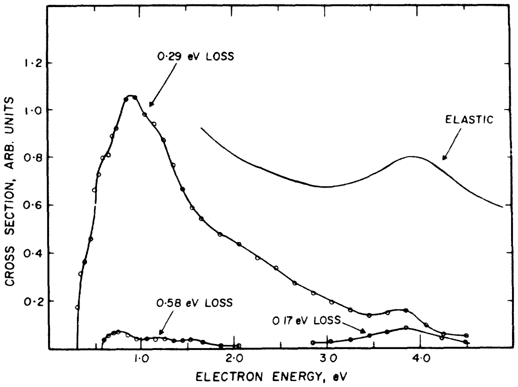


FIG. 1. Energy-loss spectrum in CO_2 at an angle of 50 deg. The known vibrational progressions are drawn in the center of the figure. The top figure is characteristic of the energy range 0.3-3.0 eV and the bottom figure is typical of the range 3.0-4.5 eV. When the angle of observation is 90 deg, no energy-loss peaks of 0.29 or 0.58 eV can be observed, but the energy-loss progression with a spacing of 0.17 eV (100 mode) is more pronounced around 90 deg.

regime of higher incident electron energies (3-4.5 eV), six equally spaced peaks are observed having a separation of 0.17 eV. This structure reaches peak intensity at an incident electron energy of 3.8 eV.

In order to facilitate interpretation, we have drawn a simplified energy-level diagram[9] at the center of Fig. 1. The CO_2 molecule has three fundamental vibrational modes, namely the asymmetric stretch mode (001, 002, etc.) with a spacing of 0.29 eV, the symmetric stretch mode (100, 200, etc.) with a spacing of 0.17 eV, and the bending mode (010, 020, etc.) with a spacing of 0.08 eV.



ENERGY DEPENDENCE OF INELASTIC AND ELASTIC CROSS SECTIONS IN CO_2

FIG. 2. Energy dependence of the 0.17-, 0.29-, and 0.58-eV (100, 001, and 002 vibrational modes) loss cross sections and the elastic cross section in CO_2. An approximate value for the 0.29-eV (001) cross section obtained by normalization to the elastic scattering from the 4-eV compound state is 3×10^{-16} cm^2. All the energy-loss cross sections are drawn on a compatible scale. The 001 vibrational energy-loss peak is unobservable around the 90-deg angle of observation, indicating that a *p*-wave compound state is involved. Pressure-dependence measurements show that the observed cross section is independent of pressure. The electron energy scale has been calibrated using the 19.3-eV helium resonance, and is accurate to ±0.1 eV. The 0.17-eV loss process around 3.8 eV is representative of all six members of the symmetric stretch modes.

We associate the 0.29- and 0.58-eV energy-loss processes observed in the low-energy regime (around 1.4 eV) with the formation of the 001 and 002 states of CO_2. The sequence of energy losses in the high-energy regime (around 3.8-eV incident energy) has a spacing of 0.17 eV, and therefore we feel that this represents mainly excitation of a series of symmetric stretch modes (100, 200, etc.). Undoubtedly, some asymmetric-mode contribution (which cannot be resolved from the symmetric mode) is also present.

Figure 2 shows the energy dependence of the 0.29-, 0.58-, and 0.17-eV loss peaks (001, 002, and 100 vibrational excitation) as well as the energy dependence of the elastic cross section.

The peak in the elastic cross section around 4 eV, first observed by Ramsauer and Kollath[10,11] and recently studied by Boness and Hasted,[4] is also shown.

The data of Fig. 1 and Fig. 2 together with the observed angular dependences and magnitude of the cross section (much larger than predicted by the Born approximation) lead us to an interpretation of the data in terms of two compound states, CO_2^-. The low-lying compound state leads to the 001 and 002 vibrational excitation with a peak at 0.9 eV. Another compound state, centered around 3.8 eV, is assumed to be too short lived for the molecule to be bent during the lifetime of the compound state. Thus, the charge distribution in the negative ion will have mirror symmetry with respect to a plane passing through the carbon atom and lying perpendicular to the molecular axis. The resulting symmetric electric field should favor excitation of the symmetric stretch mode.

Our angular measurements indicate that the elastic scattering in the region of the 3.8-eV compound state is isotropic. The formation cross section for the compound state Q_0 is assumed to be equal to its theoretical maximum[12]; i.e., $Q_0 = 4\pi\bar{\lambda}^2(2l+1)$, where $\bar{\lambda} = \lambda/2\pi$ and λ is the electron wavelength, and l is the quantum number specifying the angular momentum of the scattered electron[11] ($l = 0$, 1, 2, etc., units of angular momentum corresponding to s, p, d partial waves, respectively). Since the isotropic nature of the elastic scattering implies predominantly s-wave scattering, we set $l = 0$ and we have $Q_0 = 4\pi\bar{\lambda}^2 = 1.2\times10^{-15}$ cm^2 at 3.8 eV. Inspection of Ramsauer and Kollath's[10,11] data shows that in the vicinity of 3.8 eV the total cross section does show a variation of 0.9×10^{-15} cm^2 which is consistent with the value for Q_0 obtained above, assuming s-wave scattering.

This 3.8-eV compound state appears analogous to the 2.2-eV compound state in H_2 which has been shown to lead also to decay[13] into $H^- + H$. Similarly, O^- formation from CO_2 has been previously observed near its theoretical threshold.[14] Using the expression[15,16] $Q_- = Q_0 \exp(-\bar{\Gamma}\tau/\hbar)$, where Q_- is the negative-ion cross section, Q_0 the formation cross section for the compound state, $\hbar/\bar{\Gamma}$ the mean lifetime of the compound state, and τ the stabilization time, we can calculate the mean width of the compound state $\bar{\Gamma}$, using the values[14] $Q_- = 1.5\times10^{-19}$ cm^2, $Q_0 = 1.2\times10^{-15}$ cm^2 (derived above), and $\tau = 10^{-14}$ sec. We obtain a value for the mean width, $\bar{\Gamma} \cong 0.6$ eV, which corresponds to a lifetime of the compound state 1×10^{-15} sec, in reasonable agreement with the observed width.

The present experiment does not permit direct evaluation of absolute cross sections. Therefore, normalization methods must be employed. In order to calibrate the inelastic cross section from the partial elastic cross section, we need to know the angular distribution of scattered electrons for both processes. Our preliminary angular-distribution experiment indicates that the 001 cross section has a predominantly p-wave behavior and that the elastic cross section via the 3.8-eV compound state has an s-wave character. Thus, normalizing the differential 001 cross section to the partial elastic cross section due to the 3.8-eV compound state, and including a factor[17] of 0.9 to take into account our angle of observation (50 deg) and the p-wave nature of the 001 scattering, we obtain a magnitude of 3×10^{-16} cm^2 for the 001 cross section at its peak.

Hake and Phelps[18] derived vibrational cross sections from transport coefficients in CO_2, based on a previous experiment using a double electrostatic analyzer. However, our present experiment is more reliable than the previous one, owing to improved gas handling techniques and better flexibility of observation at different angles. The 0.08-eV energy-loss process shown by Hake and Phelps and associated with the 010 mode is not observed in the present experiment, probably because our sensitivity for such small energy losses is reduced by the presence of the elastic scattering peak. In fact, Stamatović and Schulz have investigated this problem using a combination of the trochoidal monochromator[19] and SF_6 scavenger[20] technique. With their high resolution and high threshold sensitivity, they observe energy losses corresponding to all three fundamental vibrational modes at their respective thresholds.[21]

At low electron energy (around 1 eV) the dominant energy-loss mechanism is excitation of the 001 vibrational level (upper laser level of the CO_2 laser), and the cross section to the 100 level, i.e., the lower laser level, is negligible. Thus, population inversion by electron impact (and therefore laser action at 10.6 μ) is favored in this energy region. In the region of 4 eV, laser action is likely to be suppressed since population inversion is reduced by the diminished cross section for the 001 level and the greatly enhanced cross section for the lower laser level,

100. Thus, by choosing the proper E/p (ratio of the electric field to pressure) in a discharge, it seems likely that laser action in pure CO_2 can be optimized when the average electron energy is around 1 eV. Actually, laser action by direct electron impact on CO_2 has been reported in the literature.[22]

In conclusion, our data may be successfully interpreted in terms of the compound-state model by invoking two such states. The upper state centered around 3.8 eV is believed to be short-lived, having a lifetime $\cong 1\times 10^{-15}$ sec, and is clearly observed as a pronounced peak in the elastic scattering cross section which exhibits an isotropic angular dependence. This latter observation requires further verification. This state is also observed to lead to vibrational excitation of the symmetric stretch mode of the electronic ground state of CO_2, and may also be satisfactorily applied to interpret the dissociative attachment cross section in this energy region.[23]

The lower lying state is less well understood since the experimental observations are neither as comprehensive nor as informative as those for the upper state. Hence, the details are correspondingly more difficult to extract. Since the 001 vibrational cross section is observed at threshold and rises very rapidly, the state must be low lying. The absence of structure in this cross section suggests that the state is short-lived, but probably longer lived than the upper state, since decay into the asymmetric stretch mode is observed. The absence of symmetric stretch excitation comparable in magnitude with the asymmetric stretch mode is puzzling and requires further theoretical interpretation. As pointed out, this fact favors low-energy laser operation in CO_2 at 10.6 μ by direct electron impact. Finally, preliminary angular dependence measurements indicate a p-wave nature for the 001 cross section. Future investigations will be concentrated on establishing the correct angular scattering dependences for both of the compound states in question, because the present angular dependence experiment is not as precise as we would like.

Thanks are due to A. Herzenberg, J. B. Fenn, P. D. Burrow, D. Spence, and A. Stamatović for advice on various aspects of the present work. Also, the authors wish to thank the Westinghouse Research Laboratory for components used in this experiment, and to acknowledge the assistance of W. J. Uhlig and J. H. Kearney in the construction of the apparatus.

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*Work supported in part by the National Science Foundation, DASA through Army Research Office (Durham), and Advanced Research Projects Agency.

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