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Strong mode dependence of the 3.8-eV resonance in CO_2 vibrational excitation by electron impact

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We have made a systematic observation for integrated cross sections that vibrational excitation modes are found to show quite different energy dependence in the 3.8-eV shape resonance peak in a CO_2 molecule. This feature arises from the different interaction scheme for excitation to each mode, i.e., the weak polarization interaction for excitation to the symmetric stretching mode, weak dipole interaction to the bending mode, and strong dipole interaction to the asymmetric stretching mode. The asymmetric stretching shows a sharp increase in differential cross sections (DCSs) toward small-angle scattering due to the strong dipole interaction, which washes out resonance features seen at intermediate angles. DCSs for the symmetric and bending modes clearly show conspicuous features at a wide range of the scattering angle around 3.8-eV shape resonance.

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The carbon dioxide (CO_2) molecule remains one of the most important molecules for our daily life, planet, and galaxy [1], and a study to learn a variety of dynamical aspects of CO_2 through photon, electron, or ion impact has still been very active and constituted an important part of basic physics and chemistry [1]. Vibrational excitation of the CO_2 molecule, which is the dominant energy-loss process of incident electrons and ions below about 10 eV, is an important process in applications for atmospheric phenomena, gaseous discharge, astrophysics, and others [2]. However, very little is known of dynamical aspects for the individual vibrational excitation process, i.e., the symmetric stretching (100) mode, bending (010) mode, and asymmetric stretching (001) mode. The presence of a strong resonance peak at 3.8 eV has been known and well studied, which was interpreted as due to a Π_u shape resonance. And this resonance is also known, without much reason, to qualitatively enhance excitation to the symmetric stretching and bending modes, but not much to the asymmetric stretching mode [3]. However, investigations based on experimental and theoretical means in the past have not been systematic and have used less fine energy points, hence lacking detailed information on dynamics and cross sections. A precise knowledge of excitation mechanisms and cross sections is essential for laying the basis for very accurate spectroscopic measurements and other applied sciences. An earlier study on vibrational excitation processes by electron and positron impacts in the energy region from 2 to 6 eV has found a strong mode dependence for vibrational excitation between these two projectiles [4]; and it is extremely interesting and important to examine if any mode dependence can be seen within electron impact only.

Historically the resonant peak centered specifically around 3.8 eV has been extensively studied over the years, and the works relevant to the present study are inclusive: Boness and Schulz [5], Cadez *et al.* [6], Currell and Comer [7], and more recently Cartwright and Trajmar [8]. Those measurements for vibrational excitation function by Boness and Schulz and Casdez *et al.* could not distinguish the (020) and (100) modes. For the impact energies above 4 eV, however, vibrationally inelastic differential cross-section (DCS) measurements have been limited to only two cases near room temperature. One was performed by Register *et al.* [9] for scattering angles from 10° to 140° at impact energies of 4 (only one energy around the resonance regions), 10, 20, and 50 eV only. The other was by Johnstone *et al.* [10] for only one scattering angle at 20° in the energy region from 1 to 7.5 eV. These are important studies, but they have not systematically studied the three fundamental modes independently, i.e., they have not fully covered both energy and scattering angle regions around the resonance.

In this paper, we report a systematic experimental observation of the detailed dynamics for three individual vibrational modes treated separately in the energy range from 1.5 to 6 eV with scattering angles of 10° to 130° and of the strong mode dependence in the enhancement from the 3.8-eV shape resonance. Theoretical investigations based on the close-coupling and continuum multiple-scattering methods were also performed to provide the rationale for these findings.

The experimental arrangement and procedures used in the present DCS measurements were similar to those in previous studies [11]. Briefly, electrons from a hemispherical monochromator intercept an effusive beam, and then scattered

electrons are energy analyzed in a second hemispherical system. The molecular beam is produced by effusing CO_2 through a simple nozzle that is heated to a temperature of about 50 °C to reduce contamination. The analyzer can be rotated around the scattering center covering the angular range from $-10°$ to 130° with respect to the incident electron beam. During the present measurements, overall energy resolutions are about 30 meV full width at half maximum with care being taken to ensure that the base width of the spectrum is as symmetrical as possible, and angular resolutions are about $\pm 1.5°$, respectively. Thus the energy resolution is not sufficient to resolve the rotational excitations and adjacent vibrational bands (including three fundamental modes and their overtones) of (020) and (001) as well as of (030), (110), (001), (040), and (120). The spectral decomposition similar to that described earlier [12] is also employed.

Briefly, apparatus functions for the fitting are estimated from the elastic DCS peak of He and are assumed to be Gaussian profiles (equal widths), which was found to give a near perfect fit to each energy-loss feature. The incident electron energy is calibrated with respect to the 19.3-eV resonance of He and, for vibrational excitations, to the $^2\Pi_g$ resonances of N_2. Cross sections were normalized to the elastic cross section [13] by using the measured inelastic-to-elastic intensity ratios. Experimental errors are estimated to be 30% for vibrational excitation cross sections.

The two-state vibrational close-coupling (CC) method, which includes the ground and first excited states for each vibrational mode, was employed in the theoretical investigation [14]. The fixed-nuclear orientation approximation was adopted. Interaction potentials were composed of static, exchange, and correlation-polarization terms, which were determined by using the multicenter target wave function [14,15]. The coupled differential equations were solved numerically, and the *S* matrix was extracted. Then the cross sections were calculated in a conventional manner by ensuring the convergence with respect to partial waves.

The continuum multiple-scattering (CMS) method [16] was also employed as a supplemental tool for carrying out the analysis. This method is based on a crude approximation, but is simple, and complex calculations can easily be handled. Therefore, by changing and tuning interaction potentials, we can readily repeat the calculation for reproducing experimental results, which, in turn, enables us to shed light on underlying dynamics.

Figure 1 displays results in the energy dependence of partially integrated cross sections for all three vibrational modes separately. These results were obtained by integrating experimental differential cross sections over scattering angles in the angle region between 20° and 130°. Hence, the strong dipole contributions to the cross sections are excluded. Two very interesting and prominent features emerge: (i) The symmetric stretching and bending modes show strong enhancement due to the shape resonance at 3.8 eV, while almost no enhancement at the same energy region is seen in the asymmetric stretching mode; and (ii) the peak positions for the symmetric stretching and bending modes are found to be slightly different. A similar energy dependence for the (020) mode is due to the resonance feature originating as the (010)

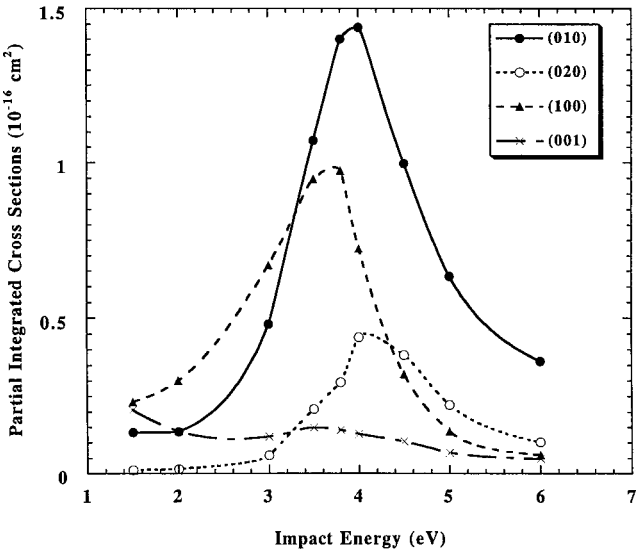

FIG. 1. Experimental integrated cross sections for the symmetric stretching (100), bending (010) and (020), and asymmetric stretching (001) modes. Note that the cross sections were determined by integrating the DCS over the scattering angles between 20° and 130°.

vibrational enhancement, but having smaller cross sections in magnitude. Below 3 eV, the (100) mode takes over the (010) mode. However, at much lower energies, this situation may well be reversed because of the strong forward peak for the (010) mode due to the dipole moment, as shown below.

Figure 2(a) shows the theoretical results obtained by the present CMS and CC methods; and those by the CMS method, which limits the integration range within 20° to 130°, i.e., partially integrated cross sections, are illustrated in Fig. 2(b). Note that the original results by the CC method, which has no adjustable parameter, give the peak position at around 5.5 eV and hence, as shown in the figure, the CC results are shifted by 1.6 eV to match the experimental peak position. The potential used in the CMS method is adjusted to reproduce the experimental peak of the (010) excitation. However, the general characteristics between the two theories agree well in magnitude and, more importantly, are in good qualitative accord for the energy dependence. Therefore, it is shown that essential features in the experiment mentioned above are well reproduced.

Although a delicate combination of the short-range and long-range interactions plays a crucial role as a whole in causing the resonance in a complex manner, the short-range interaction should be more dominant, in general, for the resonance. Resonant features in vibrational excitation proceed through such a critical change and a balance of the charge distribution of the molecule. The main differences in long-range interactions that are responsible for directing vibrational excitation for these three modes are weak polarization interaction for the symmetric stretching (100) mode [17], weak dipole interaction for the bending (010) mode [17], and strong dipole interaction for the asymmetric stretching (001) mode [17]. A swarm experiment [18] shows that the magnitude of the (001)-mode excitation cross section is the largest

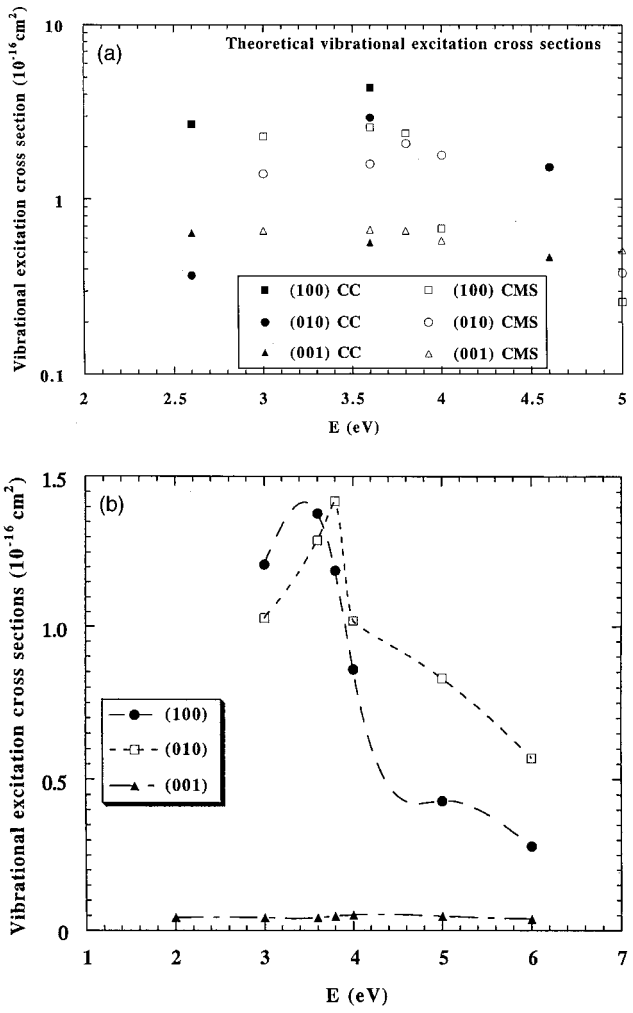

FIG. 2. (a) Theoretical integrated cross sections for the symmetric stretching (100), bending (010) and asymmetric stretching (001) modes. Solid symbols are by the CC method and open symbols are by the CMS method. Note that the CC results are shifted by 1.6 eV to match the experimental resonance peak. (b) Theoretical integrated cross sections for three vibrational modes. These were obtained by integrating the CMS-DCSs over the scattering angles between 20° and 130° for comparison with the experimental data.

among three, except for the resonance region. That it decreases as the impact energy increases is clearly consistent with the Born prediction, in which the dipole dominant transition is expected to occur. Furthermore, the strong forward peak due to the strong dipole interaction in fact governs the magnitude of the integrated cross section, and the smallest cross section for the (001) mode seen in Figs. 1 and 2(b) is because the coverage of the integration for the DCS from 20° to 130° misses the major contribution to the integrated cross section. Therefore it can be considered that the partially integrated cross sections shown in Figs. 1 and 2(b) easily contrast contributions from the resonance, while those in Fig. 2(a) are the sum of vibrational excitation through the *resonance* and those of *direct excitation* such as through long-range dipole interaction.

For a better understanding of these differences in dynamics, experimental as well as theoretical DCSs were examined,

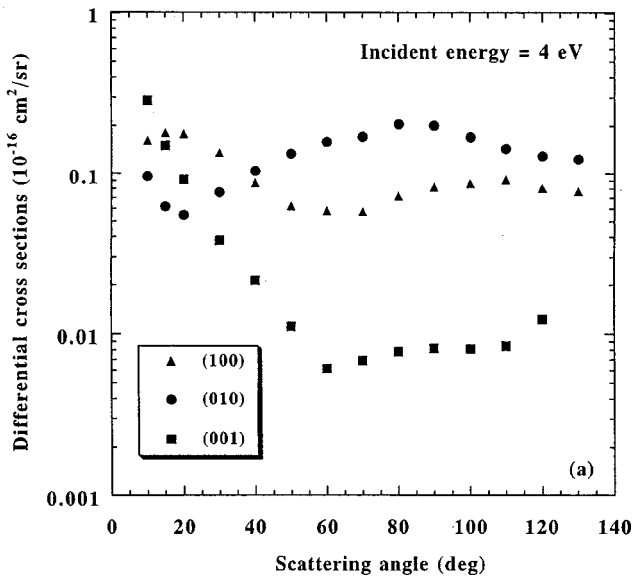

FIG. 3. Experimental differential cross sections for the symmetric stretching (100) mode, bending (010) mode, and the asymmetric stretching (001) mode at the impact energy of 4 eV.

and the present measured DCSs are illustrated in Fig. 3. Note that the present DCSs for the (010) excitation at 4 eV agree well with those of Register *et al.* The sharp increases in the DCS toward smaller angles for both (010) and (001) modes are due to the dipole moment, as already mentioned above, which may smear out the resonant enhancements in the integrated vibrational cross sections. On the contrary, the DCS for (100) mode prevails with a decreasing trend toward smaller angles around the 10–20° region due to the polarization effect and a shallow minimum around 60° with the flattening region and a comparable magnitude with the (010) mode. DCSs for the (010) and (100) modes apparently change their general shape as well as the magnitudes between the resonant and nonresonant regions. It should be noted that the recent study by Cartwright and Trajmar [8] suggests a possible contribution of the core-excited Feshbach resonance at 4–5 eV to the bending (010) mode. The result from their proposed mechanism is not in contradiction to the present result. By disassembling the measured DCS into two components for small ($<20°$) and large ($>30°$) angles and analyzing them, they have derived the symmetry-forbidden argument for an odd number of vibrational quanta for the bending excitation. However, the present experiment shows that there is no significant difference in the bending-mode excitation between an odd and even number of vibrational quanta, as exemplified in Fig. 1. Therefore, we believe that the present model based on features of potentials is more straightforward and simple, and provides a general interpretation of the observation.

The (010) DCSs show just a monotonic decrease in logarithmic scale from forward scattering angle at 20° without much undulation. For the (100) excitation mode, the flattening feature at whole angles measured remains in all energies below the resonance. In addition, the general feature in all the (001) DCSs is quite similar for each, regardless of the impact energy, i.e., a sharp decrease from 0°, followed by a

small dip which moves to lower angle as the impact energy increases. Then the flattening region prevails at larger angles $>60°$. This feature also substantiates our argument that there is no strong resonance in the (001) mode. Hence, there should be a critical dipole moment, in which it is able to wash out the resonance peak in the vibrational excitation cross section. In other words, a relatively large number of partial waves contribute to the (001) excitation, and even if one or two particular partial waves show the weak resonance feature, it is eventually smeared out when they are transformed into the integrated cross section.

As clearly revealed in Fig. 1, the small difference in the resonance peak between the (100) and (010) modes should be expected to exist, and the origin of the difference is the effect between the weak polarization interaction for the (100) mode and weak dipole interaction for the (010) mode. The weak dipole interaction, which is still stronger than the polarization interaction, results in the long-range effect on the target causing the increase in DCSs at small scattering angles, while the polarization interaction is short range compared to the dipole interaction and the influence on the scattering at large distance is weaker. This difference in the interactions causes the small difference in the peak position between the two. The position of the (100) peak appears to be lower than that of the (010) peak, as stated before. The position of the shape-resonance peak should be controlled by the delicate combination of short- and long-range interactions. Therefore, the position peak for each mode does not necessarily occur at the same energy. The static and exchange interactions, which consist mostly of a short-range interaction, are the main source causing the resonance. The static, and exchange interactions differ for each vibrational mode slightly because the nuclear-coordinate dependence of the molecular charge distribution slightly differs from one mode to another. And this small change in the short-range interaction undoubtedly results in the change in appearance of the resonance. However, within our model, the difference in the long-range interaction among three vibrational modes is much stronger and more significant than that in the short-range interactions. Hence, the long-range interactions for three modes appear to control the general feature of the cross section near the resonance. A good understanding of this mechanism should be significant in attempting the finer spectroscopic measurement and analysis.

The features we have observed here should be common to the majority of nonpolar molecules where the dipole moment is induced when either the bending or asymmetric modes are excited; and hence the present study provides a guideline for much precise spectroscopic analysis.

In summary, we have experimentally observed and theoretically rationalized that there is no peak due to the resonance in the vibrational excitation cross section for the asymmetric stretching (001) mode, while the symmetric stretching (100) mode and bending (010) mode do show a strong enhancement at around 3.5–4 eV in cross sections due to the shape resonance. However, the peak positions for the (100) and (010) modes appear to be different because of the sensitive combination of short-range and long-range interactions. These phenomena were interpreted as the effect of weak polarization interaction for the (100) excitation, weak dipole interaction for the (010) excitation, and strong dipole interaction for the (001) excitation.

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