Mode Dependence in Vibrational Excitation of a CO_2 Molecule by Electron and Positron Impacts

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We have found theoretically, for the first time, that vibrational excitations of a CO_2 molecule by electron (e^-) and positron (e^+) impacts are strongly dependent on the charge of the projectile at impact energy below 6 eV. For the symmetric-stretching mode, the excitation cross section of e^- impact is larger by 2 to 3 orders of magnitude than that of e^+ impact, while for bending and asymmetric-stretching modes the magnitude of both cross sections for e^- and e^+ impacts is nearly comparable. These results are qualitatively confirmed experimentally, and are interpreted as the difference of interactions and incident e^- or e^+wave functions. [S0031-9007(98)05939-0]

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A comparative study of electron (e^-) and positron (e^+) scattering from atoms, molecules, and condensed matter is known to provide a fundamental knowledge of underlying physics for electronic structure and scattering dynamics, and hence, is important for atomic physics, condensed matter physics, and nuclear physics [1]. In addition, this knowledge helps in understanding physics for other collision processes which involve different types of exotic particles. Total cross sections by e^+ impact on atoms and molecules are known to give smaller values than those for e^- impact below about 100 eV to a few eV region, and this feature has been interpreted as a result of cancellation of static and polarization potentials for e^+ impact while these potentials are added up, along with the additional exchange interaction for e^- impact, thus causing the stronger interaction. For specific inelastic processes, unfortunately, very few systematic studies by e^+ impact have been performed for gaseous targets, and a detailed comparative study between e^- and e^+ impact is virtually nonexistent except for some preliminary investigation of experimental results for rare-gas atoms and simple molecules [2]. Only recently, Gianturco and colleagues [3(a)] have carried out a careful study on e^+ scattering from CO_2 molecule for elastic as well as vibrational excitation processes for the symmetric stretching mode, and have compared it with their previous study [3(b)] for e^- scattering in order to shed some light on the coupling mechanism.

Earlier in our study [4], we have observed that the total cross section for CO_2 for e^- impact is indeed larger by 40% than that for e^+ impact below 100 eV or so, and continues to be so until the impact energy reaches down to 3 eV. Below 3 eV, however, the magnitude of the cross section is found to reverse, i.e., the total cross section for e^+ impact becomes larger by 25%, although it reverses again at much lower energy around 0.5 eV. At the time, we speculated a possible cause for this phenomena as being due to anomalously large cross sections for either rotational or vibrational excitation, or both for e^+ scattering. An exploratory study for rotational excitations by both projectiles was reported some time ago by Takayanagi and Inokuti [5] based on the Born approximation, who showed that for a molecule with a negative quadrupole moment, rotational excitation cross sections of e^+ impact should be larger than that of e^- impact, at least near threshold. It can be shown that for vibrational excitation, the situation is almost the same, and the Born theory gives a larger cross section for e^+ impact for a molecule which has a negative quadrupole moment at near threshold. The realization of the distinction in the interaction scheme and dynamics between two projectiles is significant. These observations have quickly led us to jointly investigate the difference in vibrational excitation mechanisms for e^- and e^+ scattering at low energies as we report here.

We have studied vibrational excitation processes of CO_2 for symmetric-stretching, bending, and asymmetric-stretching modes for e^- and e^+ impacts based on a close coupling method and the continuum multiple scattering (CMS) method. Furthermore, we have conducted an experimental study to measure the energy-loss spectrum by the sum of all vibrational modes in order to examine our theoretical results.

Here, we are now concerned with only vibrational excitation and elastic processes below the positronium formation threshold energy (6.7 eV) since below this energy, no electronic excitation channel is known to exist. In our close coupling method, two vibrational-channels within the fixed-nuclei orientation approximation are adopted. The interaction potentials include the static, exchange

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(electron impact only), and correlation-polarization potentials. The static potential was determined from SCF wave functions obtained by the GAMESS program [6], and the exchange potential was represented by the Hara-type free-electron gas potential, while the correlation-polarization potential was constructed by matching the asymptotic polarization and correlation at a shorter distance [7]. Then, the coupled equations were solved numerically. Furthermore, we have carried out the calculation based on the CMS method to further examine vibrational excitation dynamics [8]. The CMS treats a continuum-electronic state in molecular field which is divided into three spatial regions of interaction: atomic, interstitial, and outer regions within the fixed-nuclei approximation. By changing intranuclear distance of the target molecule and repeating the calculation, vibrational excitation processes can be handled approximately [9].

We summarize some of the characteristics of the interaction scheme of both projectiles. For e^- impact, the static and correlation-polarization interactions are both attractive, and the exchange interaction is known to play an important role when the incident e^- energy is low. These three interactions contribute in a rather complex manner to scattering processes. For e^+ scattering, the static interaction is repulsive and the correlation-polarization interaction is attractive, but no exchange interaction exists. Hence, the repulsive static and attractive polarization cancel out, resulting in the smaller interaction on scattering at low-to-intermediate scattering energies, as we have witnessed in the total cross section [3]. It is important, and also our present aim, to examine how these interaction potentials contribute to specific modes in vibrational excitation processes.

The present experimental apparatus and procedure for the energy-loss (EL) measurement have been discussed in detail in our previous papers [10(a)], and new specific techniques developed for this particular measurement will be discussed in a separate paper [10(b)]. Briefly, both experiments by e^- and e^+ scattering were performed by using the absorption-type apparatus. The energy spectrum is obtained from the time-of-flight (TOF) spectrum. The beam source was produced by a radioisotope ^{22}Na via secondary electrons (e^- beam) and slow positron from a tungsten-ribbon moderator (e^+ beam).

In order to determine vibrational excitation cross sections using these beams, two peaks arising from unscattered peaks of the TOF spectrum in vacuum and gas runs are compared. The unscattered peak includes contributions from forward scattering components of elastic and inelastic scatterings, from which we have subtracted the pure-elastic contribution to obtain the vibrational contribution. The vibrational excitation cross section Q_{vib} is determined by using the relationship to the total cross section Q_t, viz., $Q_{\mathrm{vib}} = I_{\mathrm{vib}}(Q_t/I_s)$, where Q_t and I_s are the total cross section and the intensity of total scattering, respectively, and I_{vib} is the intensity of vibrational excitation, in which we have determined by the present energy-loss spectrum.

Specific threshold energies [11] for vibrational excitation channels considered here are

symmetric-stretching:(100)	= 0.1653 eV;
bending:(010)	= 0.0827 eV;
asymmetric-stretching:(001)	= 0.2912 eV.

Present theoretical vibrational excitation cross sections for e^- and e^+ impacts at 2, 5, and 6 eV are tabulated in Table I. We also provide the ratio of a vibrational-excitation cross section of e^- impact to that of e^+ impact for each vibrational mode. To our surprise, two sets of the cross section for the symmetric-stretching mode show an extremely strong disparity depending upon the charge of the projectile and are substantially affected particularly at intermediate energies. Hence, apparently the ratio varies widely over 3 orders of magnitude, while those cross sections for the asymmetric-stretching and bending modes are not much different for both projectiles, and hence the ratios are within less than a factor of 2 in all energies studied; these two modes are less sensitive to the charge of the projectile. Note that these variations in the symmetric-stretching mode take place over narrow intervals of the incident energy. Since the symmetric-stretching mode is coupled to the quadrupole transition, and hence has a relatively significant effect from the polarization interaction, it may be understandable to see more sensitivity to the target characteristics, while the asymmetric and bending modes are coupled to the long-range induced-dipole transition. It should be interesting to note that for the (100)- and (010)-mode excitations, the strong shape-resonance at 3.8 eV is known to be present for e^- impact, while for the (001)-mode excitation, no such strong shape-resonance has yet been observed. For e^+ impact, although no systematic study has been carried out to search any resonance, it seems unlikely judging from the shape of the total cross section that any strong resonance is present in this energy region. Because of the 3.8-eV resonance, for the bending mode, the cross sections for e^- impact are consistently larger than those for e^+ impact in the energy region we studied. On the contrary, for the asymmetric stretching mode, the cross sections for e^- and e^+ impacts are comparable, and no strong resonance is known to exist for this mode in the energy region with which we are concerned. Even taking the effect of the 3.8-eV resonance into account, it appears that the overwhelming disparity of the cross sections for the symmetric-stretching excitation is noteworthy, which leads us to a careful investigation.

To this strong mode dependence in vibrational excitations, we provide the following interpretation: When a e^- approaches to the target, an addition of an extra e^- alters significantly the target electron charge distribution, hence causing a large deformation in the electronic cloud of the molecule. This deformation

TABLE I. Vibrational excitation cross sections in unit of 10^{-16} cm^2. The notation $A(-B)$ corresponds to $A \times 10^{-B}$.

Energy (eV)	2			5			6		
Vibrational state	e^-	e^+	e^-/e^+	e^-	e^+	e^-/e^+	e^-	e^+	e^-/e^+
(100)[a]	1.8(−3)	6.4(−4)	2.8	4.3	1.2(−3)	3600	9.1(−2)	1.2(−3)	76
(010)[b]	4.7(−1)	3.3(−1)	1.4	3.8(−1)	2.6(−1)	1.5	2.8(−1)	1.6(−1)	1.8
(001)[a]	9.6(−1)	1.3	0.7	5.7(−1)	6.6(−1)	0.9	4.7(−1)	5.3(−1)	0.9

[a]The close-coupling calculation.
[b]The CMS calculation.

induces a stronger vibrational excitation. When a e^+ approaches toward the target, a e^+ is repelled and kept outside of the target electron distribution mostly by the static interaction (nuclear repulsion), resulting in the weaker interaction with nuclear motions. More rigorously, the coupled equations we solved contain a coupling term multiplied by an initial-channel continuum e^- (or e^+) wave function. For the coupling matrix element, viz., $\langle(000)|V(\mathbf{r})|(100, 010, 001)\rangle$ where $\mathbf{r}$ describes the $e^-(e^+)$-target distance, it falls off rapidly as the $\mathbf{r}$ increases, and has the same magnitude both for e^- and e^+. Therefore, the coupling will be effective only where both the coupling and the continuum wave function are of reasonable size. Since, as stated, the e^+ is repelled at small $\mathbf{r}$ by the strong static potential of the molecule, the e^+ continuum wave function is found to be small for small $\mathbf{r}$ compared to that of the e^- which is attracted, and hence, the wave function is in a normal size. Therefore, if the wave function is very small where the coupling matrix element is finite and grows to only normal size where the matrix element is small as in the case of the polarization potential, then the effective coupling becomes weak and the cross section will be small. On the contrary, if the interaction potential has a long-range nature like the induce-dipole interaction, the effective coupling will be also a long-range interaction and has the same effect both for e^- and e^+, and therefore two sets of the cross sections are similar in magnitude except for the resonance region.

It may be worthwhile examining the present results from the different point of view since the finding above appears to contradict the prediction based on the Born approximation as discussed earlier. The simple form of the Born approximation near threshold of rotational and vibrational excitation cross sections shares a similar structure and can be expressed generally as

$$\sigma(k_i, k_f, v_f, J_f) = F(k_i, k_f, v_f, J_f)[\mathbf{Q}^2 \pm \boldsymbol{\alpha}\mathbf{Q}f(k_i, k_f) + \boldsymbol{\alpha}^2 f(k_i, k_f)], \quad (1)$$

where the upper (+) sign corresponds to the e^- case and the lower (−) sign to the e^+ case. In Eq. (1), $F(k_i, k_f, v_f, J_f)$ is a function which depends only on the initial (final) momentum $k_i(k_f)$ of the $e^-(e^+)$ and rotational and vibrational quantum numbers $v_i(v_f)$ and $J_i(J_f)$. $\mathbf{Q}$ and $\boldsymbol{\alpha}$ represent a quadrupole- and polarization-interaction coupling matrix elements sandwiched by nuclear wave functions, respectively, for vibrational excitation. For rotational excitation, these $\mathbf{Q}$ and $\boldsymbol{\alpha}$ correspond merely to the quadrupole moment and polarizability of the molecule, respectively. In a harmonic oscillator approximation, the vibrational coupling matrix element can be simplified by representing a product of the derivative of the quadrupole moment and polarizability with respect to intramolecular separation $\mathbf{r}$ and the nuclear wave function overlap matrix element.

As is apparent from Eq. (1), at least near-threshold, the rovibrational excitation cross section by e^+ impact should be larger than that by electron impact, *if* the molecular quadrupole $\mathbf{Q}$ or polarizability $\boldsymbol{\alpha}$ has a *negative* value. And indeed, for some molecules such as N_2, rotational cross sections are found to become larger for e^+ impact and the difference becomes wider by a few factors as the energy increases. These rotational excitation cross sections determined by the Born formula (1) were found to agree well with those by more reliable close coupling calculations, and hence, the validity of the Born approximation has been supported [12]. However, the situation is not as clear for vibrational excitation. Some examinations for vibrational excitation by using the Born formula and close coupling show a rather poor agreement, at least at the intermediate energy region below 10 eV [13]. Hence, we believe that in the present energy region studied, our

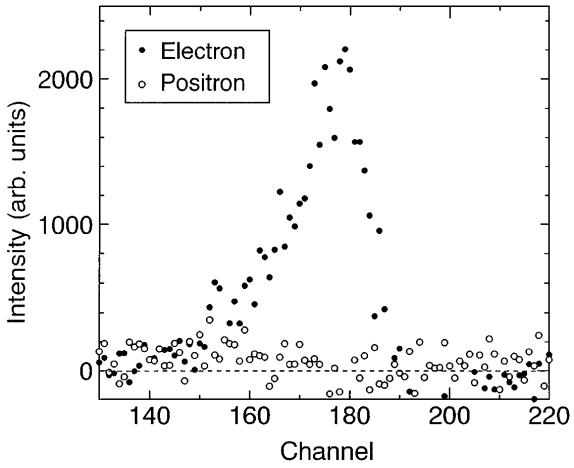

FIG. 1. Experimental energy-loss spectra by electron and positron impacts at impact energy of 6.5 eV: ●, electron impact; ○, positron impact.

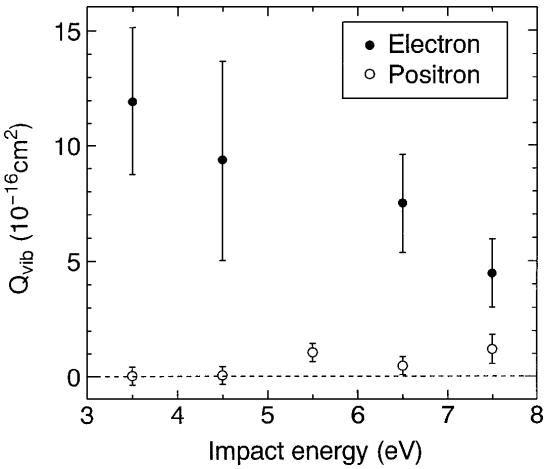

FIG. 2. Experimental cross sections for vibrational excitation (the sum of the three vibrational modes) from 3 to 7 eV impact energy.

close-coupling method gives more reliable results for vibrational excitation, in which, except for the high energy regime, the Born approximation may not offer a reliable result for vibrational excitation for e^- and e^+ impacts.

Gianturco *et al.* [3(a), 3(b)] have carried out a theoretical calculation for (100)-mode vibrational excitation by e^+ impact below positronium formation threshold down to 0.2 eV, and compared with their previous results by e^- impact. They have found the similar trend of much smaller cross section by a factor of 100 or so. Their observation is consistent with the present results for this vibrational mode.

In order for us to substantiate our theoretical findings, we have performed an experimental energy-loss (EL) measurement for these channels by e^- and e^+ impacts for a few impact energies. Typical EL spectra of positron and electron beams measured are shown in Fig. 1 [14]. Clearly, the EL spectra show that the EL spectrum for e^- impact is significantly larger by at least an order of magnitude than that for e^+ impact, qualitatively supporting our theoretical results. The present experimental cross sections, converted from these spectra, for the sum of three excitation modes are illustrated in Fig. 2. Again, the vibrational excitation cross sections for e^- impact are much larger than those of e^+ impact and show weaker energy dependence in the present energy domain.

At 5 eV, the experimental cross section by e^- impact is larger by an order of magnitude than that by e^+ impact, consistent with the present theoretical finding. The recommended vibrational excitation cross sections for e^- impact are 2×10^{-16} cm^2, 4×10^{-17} cm^2, and 5×10^{-17} cm^2 for (100), (010), and (001) vibrational modes, respectively, at 5 eV [15]. The present theoretical vibrational-excitation cross sections are in reasonable accord with these values at this energy. In the impact energy from 4 to 6 eV, no substantial change in the experimental ratios for the energy-loss was observed.

In summary, we have observed a strong vibrational mode dependence for vibrational excitation in e^+ and e^- scattering from CO_2 for the first time; for the symmetric stretching (100) mode, the vibrational excitation cross section by e^- scattering is larger by 2 to 3 orders of magnitude than that by e^+ scattering, while the cross sections for asymmetric stretching (001) and bending (010) modes are rather similar. Our experimental results are qualitatively consistent with theoretical findings. The weak quadrupole and long-range strong dipole interactions in combination with the continuum wave function are responsible for the cause. In addition, the presence of the 3.8 eV shape resonance for e^- impact also accounts for this difference to some degree.

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