Observation of Friction in the Nuclear Dynamics of CO_2^- near the Equilibrium Geometry of the Negative Ion

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Unusual excitation patterns have been observed in the two-dimensional electron scattering spectrum of carbon dioxide in the region of the 4 eV shape resonance. Certain features of the spectrum presented are explained in terms of a quantum mechanical analog of friction which acts to dampen the nuclear motion of the negative ion.

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An efficient mechanism for exciting high vibrational levels of a molecule is via the formation of a shape resonance [1]. An incoming electron attaches to the molecule forming a negative ion. The nuclear wave function experiences a new set of forces since it is now subject to the negative ion potential. After a period of time, the negative ion can decay by emitting an electron. The resultant changes in the nuclear wave function are reflected in the vibrational distribution of exit channels selected by the negative ion system. In a theoretical study of the dynamics of temporary negative ions, Domcke and Estrada [2] predicted a friction mechanism where the energy associated with the wave packet decays faster than the population. This causes the wave packet's motion to become damped.

A particularly comprehensive way to study such systems is to use a two-dimensional scanning technique [3] in which the yield of scattered electrons is mapped as both a function of electron impact energy and energy loss. From the energy-loss coordinate, the final vibration channel can be deduced, subject to resolution restrictions. For a given value of energy loss, the signal commonly varies as a function of impact energy. This provides information about the coupling of the negative ion state to the final vibrational channels.

Recently, a study of this kind was performed on vibrational excitation of carbon dioxide due to attachment of an electron of about 4 eV energy [4]. The conclusion of this study was that the negative ion wave function propagates along both the symmetric stretch and bend coordinates during the negative ion lifetime. The potentials and the initial state wave function have a C_∞ axis along the molecule. Because of the symmetry this imposes on the propagation of the wave packet, only vibrational modes of the symmetry $\sum_g$ are expected to be observed. These vibrational modes are the $(n,0,0)$-type Fermi polyads [5]. In addition to these polyads, vibrational modes due to $(n,1,0)$ polyads are observed. These vibrations possess $\prod_u$ symmetry. As has already been pointed out [4] the ratio of excitation to vibrational states of $\sum_g$ symmetry to those of $\prod_u$ is a reflection of the symmetry-breaking process only, not the general nuclear dynamics. A mechanism for lowering the symmetry restrictions on the exit channels available has been discussed by Gallup [6]. He suggest that a nonresonant s-wave may interfere with the principle partial wave of the resonance, allowing the excitation of a generally different set of vibrations. This mechanism coupled with a two-dimensional boomerang model [4,7] is able to provide a good account for low vibrational excitation via the 4 eV CO_2 negative ion shape resonance.

Such a system provides a possible candidate for observing friction. Damping in the wave packet's motion could cause it to become trapped as two separate wave packets, either side of the linear geometry on the $^2A_1$ potential energy surface. Such behavior would be reflected in the vibrational distribution of the final states excited. Any manifestation of such a phenomenon would be most prominent for excitation to very high vibrational levels, since these levels correspond to the longer-lived parts of the wave function [7], giving the friction process more time to cause a noticeable effect. In order to search for evidence of the predicted mechanism, we measured two-dimensional spectra in the 4 eV impact energy region, using carbon dioxide as the target gas, concentrating on regions of high (>1.5 eV) vibrational excitation.

The result of compiling many such spectra is shown in Fig. 1. Several rectangular regions were collected using the technique described by Reddish, Currell, and Comer [3]. These separate regions were added together digitally to produce the composite figure shown. To provide a more complete picture of the resonance system, data discussed previously [4] were included in the composition process. The dimensions of the rectangles which comprise this composite figure were carefully chosen, to concentrate the spectrometer time as efficiently as possible on the region of interest. In order to maximize the sensitivity, the differentially pumped spectrometer described by York and Comer [8] was used in conjunction with the detector of Hadfield *et al.* [9].

The general form of this spectrum is as expected for vibrational excitation via a shape resonance. A series

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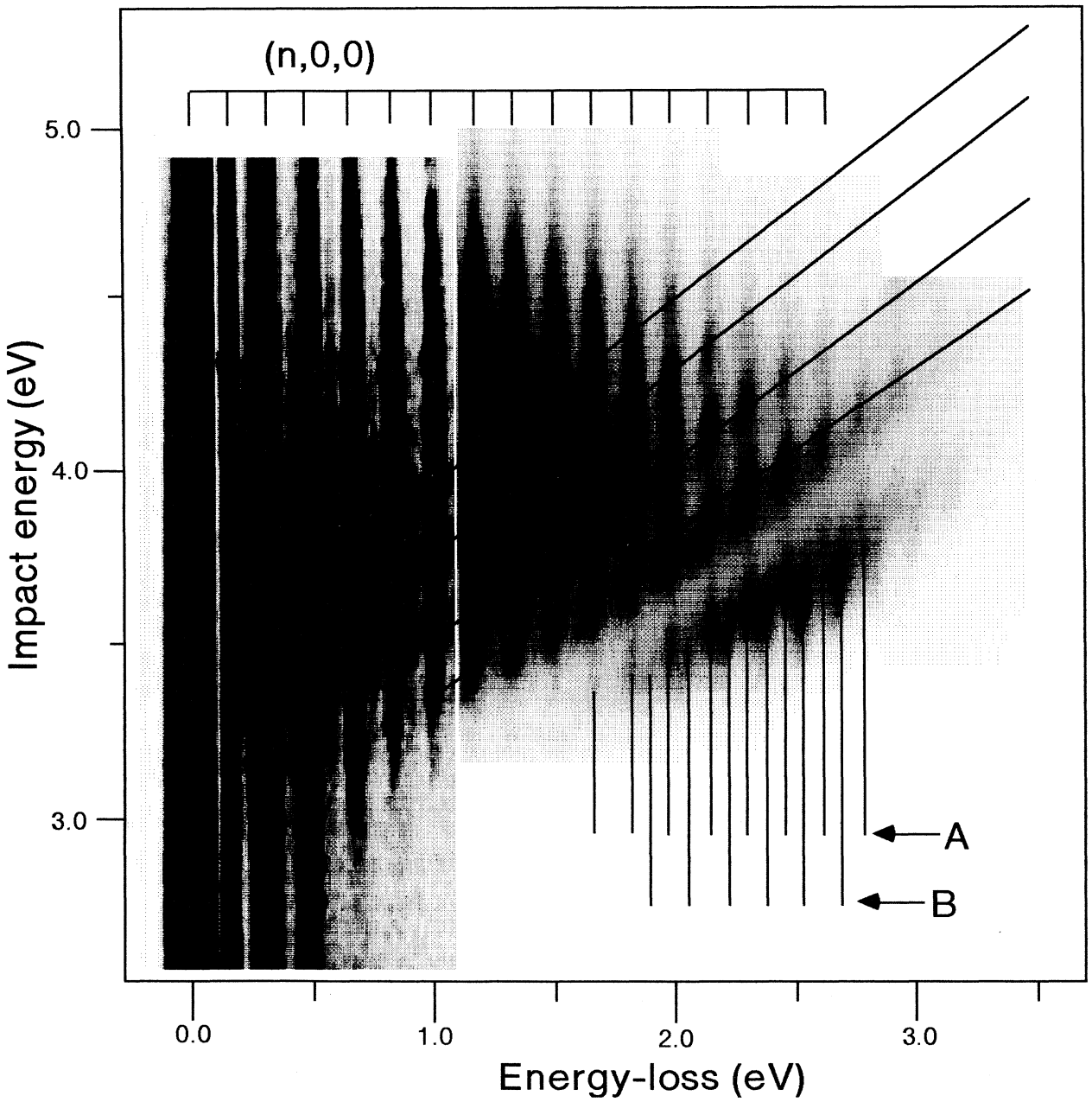

FIG. 1. A gray-scale plot showing the scattered electron intensity as a function of impact energy and energy loss, using gaseous carbon dioxide as a target. The break in the data (about 1.1 eV energy loss) differentiates scattering conditions. Data to the left of this divide were taken at a scattering angle of 20 deg, at an energy-loss resolution of about 20 meV. Data to the right were taken at a scattering angle of 15 deg, with an energy-loss resolution of about 40 meV. The "vibrational progression" shown at the top of the spectrum is included to allow comparison to previously published spectra (see text for references). The boomerang effect is emphasized by the inclusion of several diagonal lines along which maxima are observed. The new type of excitation (labeled *A* and *B*) occurs in the lower impact energy portion of the spectrum.

of vibrational excitations is observed [decay to $(n,0,0)$ Fermi polyads] with maxima which form diagonal lines typical of boomerang shape-resonant systems [10]. This is a continuation of the behavior previously discussed [4]. Above an energy loss of about 1.8 eV, a new type of excitation occurs. It is situated to the low impact energy side of the main body of excitation. Maxima are observed at half the energy-loss spacing associated with

decay of the $(n,0,0)$ polyads. Alternate maxima seem to be associated with the $(n,0,0)$ polyad progression (labeled A) and a different form of excitation (labeled B).

At such a high energy loss, neighboring $(n,0,0)$ polyads overlap. Since these states are of the same symmetry, they will interact, creating a vibrational pseudocontinuum composed of states with $\sum_g$ symmetry. A model study of the resultant vibrational wave functions [11] shows that the most linear states of the pseudocontinuum occur in regularly spaced groups. The spacing is about the same as that between the discrete $(n,0,0)$ polyads. The most highly bent states are found in groups with the same spacing, halfway between the groups of linear states. Essentially, traveling across an energy interval of about 160 meV across the pseudocontinuum, the states progressively change from being linear to highly bent (80 meV later) and then revert to being linear again.

The type A excitation appears to be an extension of the excitation already observed at lower energy loss [4]. Accordingly, we attribute this excitation to decay of fairly linear parts of the negative ion wave function. Excitation with the energy loss observed for type B excitation could be explained as either decay to linear members of the $(n,1,0)$ pseudocontinuum or to highly bent components of the $(n,0,0)$ pseudocontinuum. We will consider each mechanism in turn.

The $(n,1,0)$ pseudocontinuum is of a separate symmetry ($\prod_u$) to the $(n,0,0)$ pseudocontinuum, so members of the two pseudocontinua do not perturb each other. For every member of the $(n,0,0)$ pseudocontinuum, there is a corresponding member of the $(n,1,0)$ pseudocontinuum at about 80 meV higher energy loss. The wave function of the $(n,1,0)$ state can be derived from that of its corresponding $(n,0,0)$ state simply by adding 1 to the bending quantum number of each component of the wave function description. An identical clumping of states occurs in the $(n,1,0)$ pseudocontinuum but 80 meV later. Thus excitation is observed at the correct energy loss to be attributed to decay to the linear parts of the $(n,1,0)$ pseudocontinuum.

Such excitation would have to occur via the mechanism described by Gallup [6] due to symmetry considerations. Gallup's model predicts only a very weak energy dependence. This would result in the type B excitation having a similar relative intensity distribution (reduced by an overall multiplicative factor) to that observed in type A excitation but shifted to about 80 meV higher energy loss. This is clearly not the case in the spectrum presented. Moving from the type A maxima to higher impact energy, a second maximum of greater intensity is encountered about 300 meV later. In contrast, moving from the type B maxima, we find only a weaker peak in each case. This weaker peak appears as a shoulder to the second diagonal line of type A peaks. Furthermore, the spectrum presented in Fig. 1 is taken at a low scattering angle. The angular measurements of Danner [12] (shown in Fig. 5 of [7]) suggest that states of $\prod_u$ symmetry are not preferentially excited at low angles. Thus, decay to $(n,0,0)$ states can be expected to dominate the spectrum. These factors suggest that the type B excitation is not due to decay to linear components of the $(n,1,0)$ pseudocontinuum.

Alternatively, highly bent components of the $(n,0,0)$ pseudocontinuum could be excited, giving rise to the type B excitation observed. These highly bent states must be excited preferentially, compared to the states with an intermediate amount of bending. Otherwise, the whole of the $(n,0,0)$ pseudocontinuum would be excited, removing any structure in the energy-loss direction. This preferential excitation can be viewed as a result of the friction process predicted by Domcke and Estrada [2]. As the negative ion wave packet is subjected to the friction, it slows down, becoming trapped symmetrically, either side of the linear geometry. This trapping is expected, based on the potential energy curves of the negative ion [13]. This trapped portion of the negative ion wave function can only decay to highly bent states of the $(n,0,0)$ pseudocontinuum, resulting in the preferential excitation observed. Type B excitation is observed most intensely at the low impact-energy side of the resonance. This is predicted by the model outlined above, since the wave packet has less energy to lose during the friction process before the trapping occurs. Interference structure is still observed due to the boomerang effect, since the decay occurs before the wave packet has become stationary. The nuclear dynamics of this process could possibly be studied further within the time-dependent framework outlined by Kazansky and Sergeeva [14].

This friction mechanism is further able to explain certain features of the spectra reported by Allan [1]. At higher energy loss (3–5 eV approximately) he observed a regular series of broadened peaks occurring at characteristic energy losses. The weak incident energy dependence of the profiles observed led Allan to conclude that these features are not due to vibration of CO_2^-. These features may be due to parts of the negative ion wave packet which are subject to the friction mechanism to such a degree that they are almost stationary at an angle of about ± 135 deg (the equilibrium geometry of CO_2^-). The profiles observed would then reflect the Franck-Condon factors between the negative ion and the neutral molecule. Effectively, the negative ion has "forgotten" the impact energy as a result of friction.

The interpretation of the spectrum presented provides the first confirmation of an important quantum-mechanical effect previously predicted [2]. A more full discussion of the spectrum presented above and the friction process will be published shortly [11]. Such a mechanism could be quite general in the dynamics of polyatomic temporary negative ions. The friction traps the wave function near the equilibrium geometry of the negative ion (with appropriate symmetry imposed on the system), leading to selective vibrational excitation. In contrast, the selectivity

encountered for the usual boomerang decay is dominated by the form of the negative ion potential at the equilibrium geometry of the neutral molecule. For a polyatomic molecule, there is no *a priori* reason why these two types of selectivity should be the same. Accordingly, if the negative ion equilibrium geometry does not lie close to the trajectory of the wave packet for the first vibrational period, the friction effect may be observed in the vibrational excitation.

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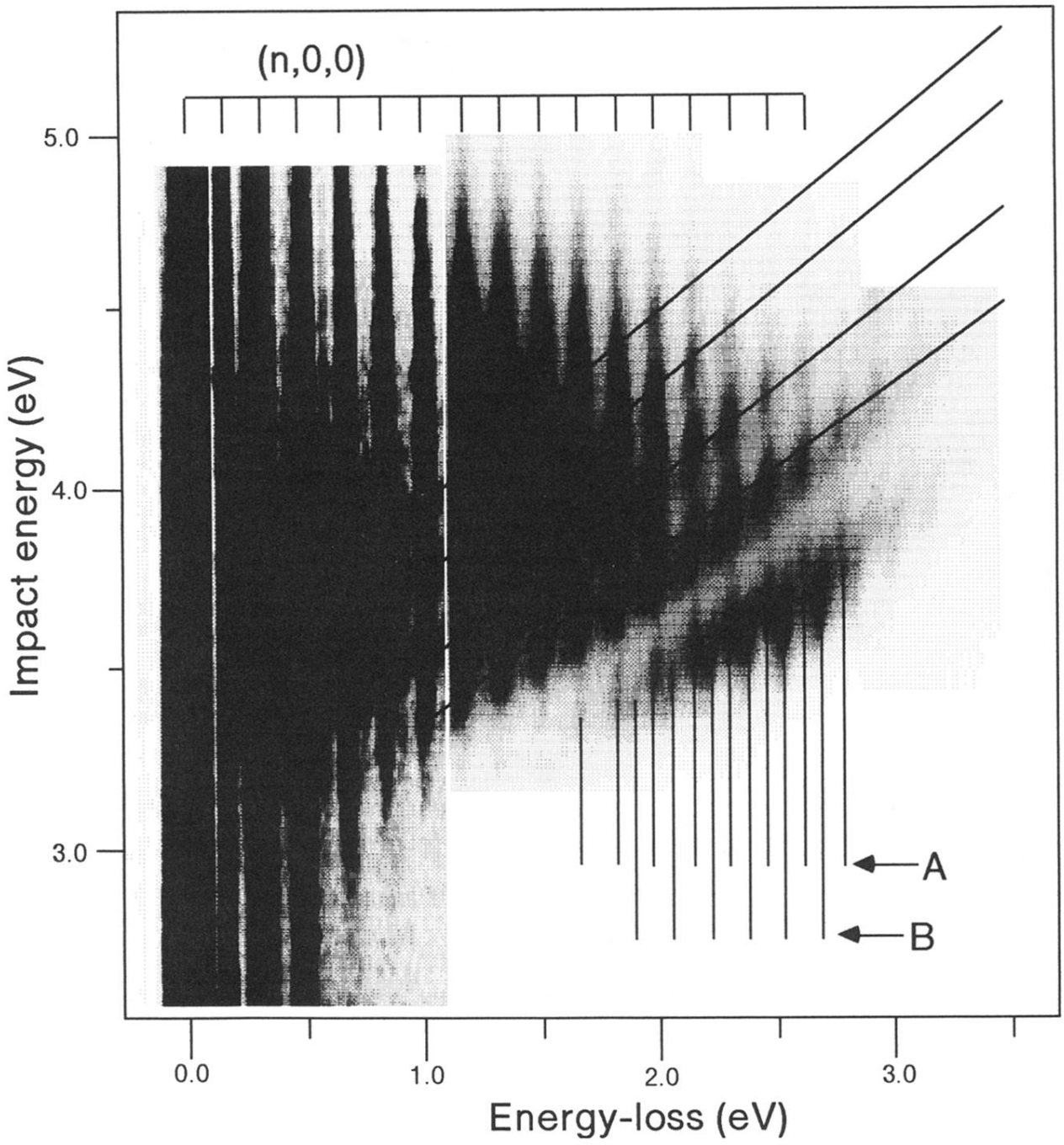

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