Virtual States and Resonances in Electron Scattering by CO_2

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The R-matrix method has been used to investigate structures observed in low energy scattering of electrons by CO_2. We are able, by directly locating S-matrix poles in the complex momentum plane, to confirm that the large threshold cross section is due to the presence of a virtual state. This is the first *ab initio* calculation to locate such a state. As the molecule is bent, we are able to follow its behavior and show that it eventually becomes a true bound state. The low energy $^2\Pi_u$ shape resonance is found to split into two components, which behave differently as the molecule is bent. [S0031-9007(98)05439-8]

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Electron scattering by carbon dioxide is of considerable interest in a variety of applications, such as atmospheric physics and gaseous electronics, and has consequently been the subject of much study. The low energy integrated cross sections have two distinctive features which, although first observed many years ago (see [1] for early references), are still not well understood. The first is a marked rise in the integrated cross section as the scattering energy decreases to zero. Morrison [2] has shown that this behavior was consistent with the existence of a virtual state of the CO_2^- system. A virtual state is not a physical state, rather it is a feature of the system, which occurs at a nonphysical energy, that profoundly influences the scattering cross sections. Mathematically, it corresponds to a pole in the scattering matrix on the negative imaginary momentum (k) axis close to the origin. Morrison's model was subsequently criticized by Lucchese and McKoy [3] who demonstrated that his polarization potential was too strong. More recent calculations [4,5] have been relatively unsophisticated and have generally omitted the very low energy region. The second feature is a resonance at about 4 eV. Cartwright and Trajmar [6] have recently argued, on the basis of the anomalous shapes of the vibrationally inelastic differential cross sections at this energy, that the resonance cannot be a simple shape resonance, as had been previously assumed, but is a composite structure which includes at least one Feshbach resonance.

We have used a new code, developed by a consortium of workers in the U.K., which uses the R-matrix method [7,8] to study electron scattering by CO_2 for energies up to 10 eV. This code includes exchange exactly and evaluates all multicenter integrals in closed form. Polarization effects and virtual electronic excitation processes are included in a completely *ab initio* manner. We included in our trial wave function, in addition to the ground state, all states having the configurations suggested by Cartwright and Trajmar as possible parents for a Feshbach resonance, i.e., $CO_2[K1\pi_g^3 5\sigma_g, \Pi_g]$ and $CO_2[K1\pi_g^3 2\pi_u, \Sigma_u^-, \Sigma_u^+, \Delta_u]$. Calculations were carried out in C_{2v} symmetry with the molecule in the yz plane. We used small complete active space configuration interaction (CASCI) wave functions, where the active space consisted of the $6a_1$, $7a_1$, $2b_2$, $4b_1$, and $1a_2$ orbitals. Such a small basis cannot give a good representation of the excited states and our vertical excitation thresholds were too high by, typically, 2 eV. This, however, has the advantage that if any Feshbach resonances are predicted by the model, then they too will be about 2 eV too high and should be clearly distinguishable from the shape resonance. The target orbitals are those of Dunning [9]. We represented the continuum electron by a basis of Cartesian Gaussians, similar to that used in [8], but have included angular momenta up to $l = 4$.

Our integrated cross sections, for the linear geometry, are shown in Fig. 1. They are compared with the experimental results of Szmytkowski *et al.* [10] and a simple static exchange calculation, which utilizes the self-consistent-field (SCF) wave function whose orbitals were used to construct our CASCI target. We also investigated a "static exchange plus polarization" (SEP) model which included short range correlation and polarization

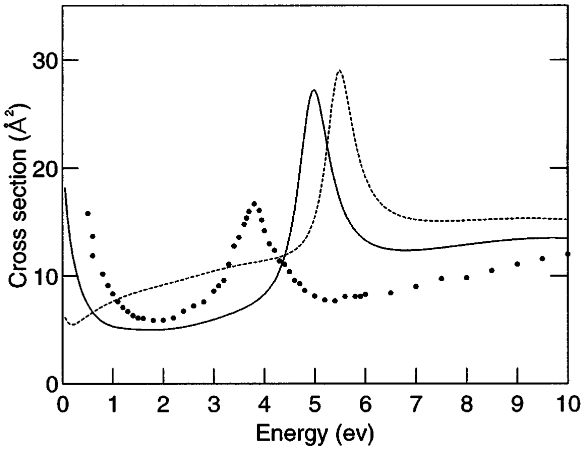

FIG. 1. Integrated cross sections. The dots are the experimental total cross sections of [8]; the solid line, our multistate elastic cross sections; and the dashed line, our static exchange results

effects. The multistate model additionally includes virtual excitations to electronically excited configurations and polarization effects due to the dipole couplings between the states. The latter are underestimates, primarily due to the omission of Π_u states, and give only about 10% of the long range polarizability. All of our models show the $^2\Pi_u$ shape resonance, but no additional resonances were found in our multistate model. All three appear to predict too high an energy for the resonance. Only the multistate model shows the marked increase in the cross section as the scattering energy approaches zero, and hence we can attribute this feature to the correlation and polarization effects omitted from the simpler models.

As noted above, the threshold spike in the cross section is characteristic of the existence of a virtual state of the anion. Polar molecules often exhibit spikes at inelastic thresholds but these can usually be attributed to "nuclear excited Feshbach resonances" [11]. Herzenberg and Saha [12] showed that a true virtual state cannot exist if a dipole potential is present, which is usually the case in molecular systems. Linear CO_2, having no dipole, is one of the few candidates. The R-matrix method is well suited to the exploration of complex momentum (or energy) space, since the scattering energy occurs simply as a parameter in the R matrix itself. In order to locate poles of the S matrix, we have to solve the scattering equations in the region outside the R-matrix sphere at complex energies and impose the appropriate outgoing wave boundary conditions. This leads to an eigenvalue problem which is solved iteratively [11]. In order to simplify the problem in the outer region, we neglect all channels corresponding to excited target states, since the scattering wave functions will be exponentially decaying and will have negligible amplitude outside the R-matrix sphere. We found, without difficulty, S-matrix poles, of $^2\Sigma_g^+$ symmetry, on the negative imaginary k axis in all three models, but only in the case of the multistate model was the pole sufficiently close to the origin to have a significant effect on the cross section. We obtained the value $k = -0.2022i$ a.u. which compares well with the value $k = -0.1620i$ a.u. which Morrison [2] obtained by extrapolating his results from real scattering energies. As expected, we find the virtual state wave function to be almost entirely s wave in nature.

It is also of interest to observe the behavior of the virtual state and the resonance as the molecule is bent. Bruna *et al.* [13] and Hopper [14], using conventional quantum chemistry techniques, found that bound states of the anion CO_2^- exist at bent geometries. The linear molecule has no permanent dipole moment, but bent configurations do. There has been much debate [12,15,16] about the fate of a bound state, in the presence of a dipole, if the binding potential is progressively weakened. In the present case, this is analogous to observing the behavior of the bent anion state as the molecule becomes linear. We started with the linear geometry and progressively bent the molecule, keeping the O-C bond length fixed at its equilibrium value. The O-C-O angles considered were in the range 180° to 145°. The behavior of the virtual state pole, in the $^2A_1$ symmetry, is shown in Fig. 2. The pole moves off the negative imaginary k axis, onto an unphysical sheet of the Riemann surface, on a trajectory well approximated by a parabola. It reaches the origin at an angle of approximately 147.5°. At larger angles, the pole lies on the physical sheet, on the positive imaginary k axis, and gives rise to a real bound state. There are also image poles, at $k' = -k^*$, which lie on another Riemann sheet and can be located using the method described by Herzenberg [17]. Herzenberg and Saha [12,17], using a very simple analytical model, studied the behavior of a state, bound by a combination of long range dipole and short range attractive potential, as the strength of the dipole is reduced. The behavior of our virtual/bound state is completely consistent with their results. They found that only for dipole moments less than 0.468 a.u. (1.19 D) did the trajectory of the virtual state reach the origin. In our model, the dipole moment is found to vary linearly with bending angle, reaching a value of 0.412 a.u. at the angle at which CO_2^- becomes bound.

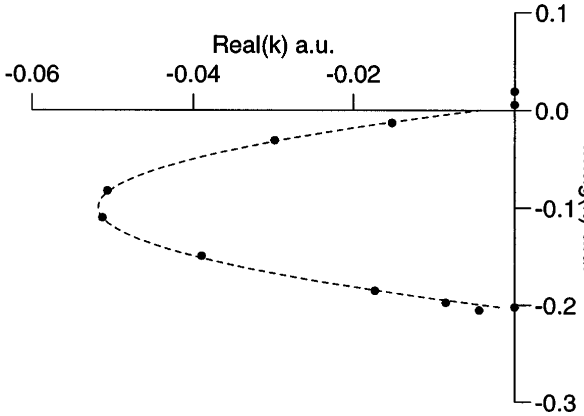

FIG. 2. Location of S-matrix poles in the complex momentum (k) plane. The dashed line is a parabola fitted to those poles lying in the lower left-hand quadrant.

The shape resonance is also expected to be affected by bending. The two components, $\Lambda \pm 1$, of the $^2\Pi_u$ state will no longer be degenerate. In C_{2v} symmetry they become $^2A_1$ and $^2B_2$ resonances. The behavior of the eigenphase sums as functions of bending angle are shown in Figs. 3(a) and 3(b). The $^2B_2$ component moves very slowly down in energy and broadens slightly. The $^2A_1$ component, on the other hand, moves down quickly and rapidly broadens. The corresponding S-matrix pole lies in the lower right-hand quadrant and follows an almost linear trajectory from $k = (0.605, -0.023)$ to $k = (0.489, -0.237)$.

The experimental results shown in Fig. 1 are total, not elastic, integrated cross sections. If vibrational motion were to be included in our model, we would expect the

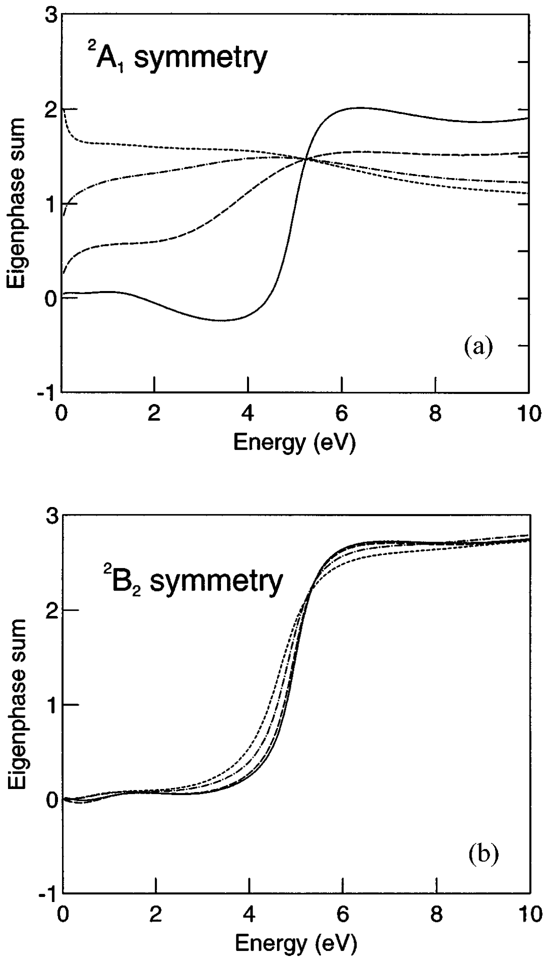

FIG. 3. Eigenphase sums for (a) the $^2A_1$ symmetry and (b) the $^2B_2$ symmetry for various bending angles. Solid line, 180°; long-dashed line, 160°; dash-dotted line, 150°; short-dashed line, 145°.

resonance to broaden and move to a slightly lower energy. We would also expect to see a marked difference between the elastic differential cross sections and those for the first few bending modes, since the $^2A_1$ symmetry would dominate the former but have little effect on the latter. In the linear geometry, the resonant state is primarily p wave with a small admixture of f wave. The dipole induced by bending will couple in a significant d-wave component. This could be the reason behind the anomalous shapes of the vibrationally inelastic differential cross sections measured by Cartwright and Trajmar [6].

We are now extending our model to use improved target wave functions and to include nuclear motion. We plan to calculate differential cross sections which can be compared quantitatively with experiment.

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