Virtual-state effects on elastic scattering and vibrational excitation of CO_2 by electron impact

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Near-threshold cross sections for elastic scattering and for excitation of the 100 symmetric stretch vibrational mode of CO_2 have been calculated using the energy-modified adiabatic phase matrix method. These calculations are based on fixed-nuclei R matrices at several internuclear geometries that incorporate short-range exchange and correlation effects. The representation of the polarization response of the target inside the R-matrix box is improved using an alternative numerical technique, the ΔR procedure. These calculations over a range of internuclear distances reveal unanticipated behavior of the near-threshold scattering matrix. A fixed-nuclei virtual state occurs only in a limited range of internuclear separation, changing to a weakly bound state outside this range. Thus an energy pole of the scattering matrix remains near threshold and has a large effect on both elastic and vibrational cross sections, but cannot be simply described as a virtual state. Our quantitative results, in good agreement with experiment, indicate that the present modified adiabatic methodology is adequate to treat this complex behavior.

Understanding virtual states and their consequences is important in a host of subdisciplines. In addition to their well-known influence on the properties of the deuteron [1], virtual states participate in current and electric-field profiles in semiconductor superlattices [2], s-wave scattering from widely used model potentials such as the von-Neumann-Wigner potential [3], and quantum wells in, for example, analysis using phase-tailored pulse trains [4].

The present paper concerns the effect of such a state on e-CO_2 scattering at energies near threshold. The continuing interest in cross sections for such collisions derives in part from their importance to molecular and chemical physics, atmospheric and plasma physics, and gaseous electronics [5]. But this system poses fundamental questions as well: e.g., an anomalously large zero-energy cross section [6–8] and a sharp peak near threshold in the cross section for excitation of the 100 symmetric stretch vibrational mode [9–12].

The first significant evidence of these anomalies was the remarkably large near-zero momentum transfer cross section determined by Lowke *et al.* [13] from transport analysis of swarm data. These cross sections were corroborated by theoretical calculations of Morrison *et al.* [6] and a virtual state mechanism hypothesized to explain them by Morrison [8]. Further evidence came from time-of-flight measurements of total cross sections by Ferch *et al.* [7]. That a virtual state, if present, might induce a pronounced threshold peak in the

$000 \rightarrow 100$ cross section was first proposed by Morrison and Lane [9] (see also [10,14]). Subsequent crossed-beam measurements by Kochem *et al.* [11] seemed to confirm this hypothesis, and contemporaraneous theoretical analysis by Estrada and Domcke [12] addressed the relationship between the virtual state and the threshold peak. Nevertheless, this hypothesis was subsequently challenged [15]. Moreover, a recent calculation [16] gave very-low-energy elastic cross sections much smaller than those of previous studies, raising serious questions about the relevance of a virtual state to e-CO_2 scattering. Finally, recent experiments by Field *et al.* [17] using a high-resolution synchrotron photoionization electron spectrometer present a significant challenge to both the measurements of Kochem *et al.* and all existing theory: for the $000 \rightarrow 100$ excitation they find a much more abrupt onset and a much smaller full width at half maximum (FWHM), noting that "it remains for example to be seen if the virtual state model is satisfactory or not." Clarifying this highly uncertain situation is the agenda of the present research.

Prior to 1985, all theoretical work on the e-CO_2 system was semiheuristic: either close-coupling calculations using empirical models for exchange and polarization [6,8–10] or dynamical theories [12] whose parameters were based on earlier theoretical work [6] and/or on experimental cross sections [11]. For near-threshold vibrational excitation, only two studies have appeared: the adiabatic-nuclear vibration (ANV) calculation of Morrison and Lane [9], which did not reproduce the structure of the peak because the ANV approximation fails to conserve energy near threshold; and the two-

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state vibrationally coupled calculation of Whitten and Lane [10], which was based on a parameterized model and not demonstrably converged. It is therefore imperative to understand vibrational excitation in this system via a more rigorous treatment that is appropriate near threshold.

Our starting point is a series of fixed-nuclei (FN) scattering calculations using R matrices in which static, nonlocal exchange, and short-range bound-free correlation effects are explicitly included [18]. By interpolation of the resulting scattering (S) matrices at real energies, we determine the pole of the S matrix as a function of the oxygen-carbon separation R_{CO}; this variation is essential to understanding near-threshold vibrational cross sections [19]. We then investigate the influence of this pole on $\sigma^{(v)}(000 \to 100)$ using the energy-modified adiabatic phase matrix (EMAP) method [20–22] to incorporate the vibrational dynamics.

A virtual (bound) state corresponds to a pole of the S matrix at momentum $k = i\kappa$ with $\kappa < 0 (\kappa > 0)$. If sufficiently near the origin, such a pole profoundly affects low-energy cross sections. For e-CO_2 scattering, it results in a zero-energy elastic cross section $\sigma^{(el)}$ whose value is exceptionally large for scattering from a nonpolar target [19]. The pole position κ is related to the zero-energy limit of the Σ_g FN eigenphase sum, $1/\kappa \equiv -\lim_{\kappa \to 0} \tan \delta_{sum}^{\Sigma_g}(k)/k$. In this limit, $\delta_{sum}^{\Sigma_g}(k)$ is equal to an excellent approximation, to the s-wave eigenphase shift $\delta_0^{\Sigma_g}(k)$, and one can determine κ by expanding the latter quantity about the pole position [8]. Doing so yields the (s-wave) scattering length $A = 1/\kappa$.

The present study uses FN R matrices calculated by Morgan [18], which are based on small complete active space configuration interaction wave functions and include a representation of polarization effects and virtual electronic excitation. We performed FN scattering calculations at R_{CO} = 1.9, 2.0, 2.1, 2.1944 (equilibrium), and 2.5 a_0. Outside the R-matrix "box" of radius $10 a_0$, we include the (local) static and polarization interactions via a power-series expansion [23].

Unfortunately, the basis used in the aforementioned FN e-CO_2 calculations positions the $^2\Pi_u$ resonance at equilibrium at 6.0 eV [18], significantly above the correct value of 3.8 eV. We have found that this error arises from the inability of the basis to correctly represent the polarization response *inside the R-matrix box*. We have developed a different procedure—the "ΔR procedure" (DRP) [24]—which we here use to correct these R matrices so as to reproduce the experimentally determined e-CO_2 scattering length [25]. The DRP begins with construction of a set of effective R matrices at an effective target radius r_0 by propagating FN variational R matrices inwards from the box radius, using as the potential energy one's best estimate of the effective potential in the near-target region from the original FN variational calculations. One then propagates each effective R matrix outward from r_0 to r_1, using a local potential, based either on theory or experiment, designed to represent more accurately the polarization response in the near-target region. Comparing EMAP and DRP results reveals the sensitivity of e-CO_2 scattering quantities to the polarization response in this near-target region. Figures 1, 2, and 3 illustrate this point by com-
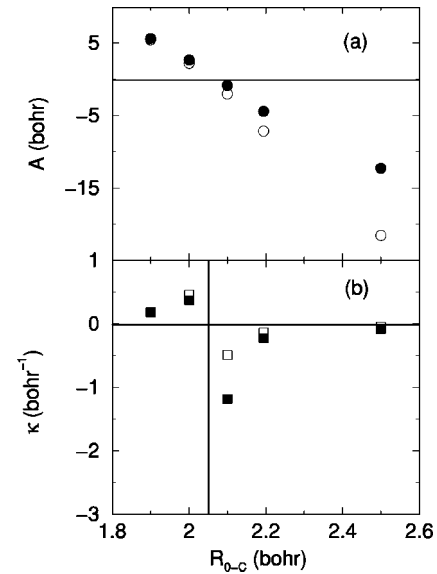

FIG. 1. Variation of (a) the scattering length A (circles) and (b) the pole position κ (squares) as a function of C-O internuclear separation. The open symbols are DRP-corrected values; the closed symbols are uncorrected.

paring uncorrected and DRP-corrected results.

An FN K matrix was computed from each FN R matrix using standard procedures. This determines the complex energy of an S-matrix pole near the continuum threshold as a function of R_{CO}. The values of these parameters are sensi-
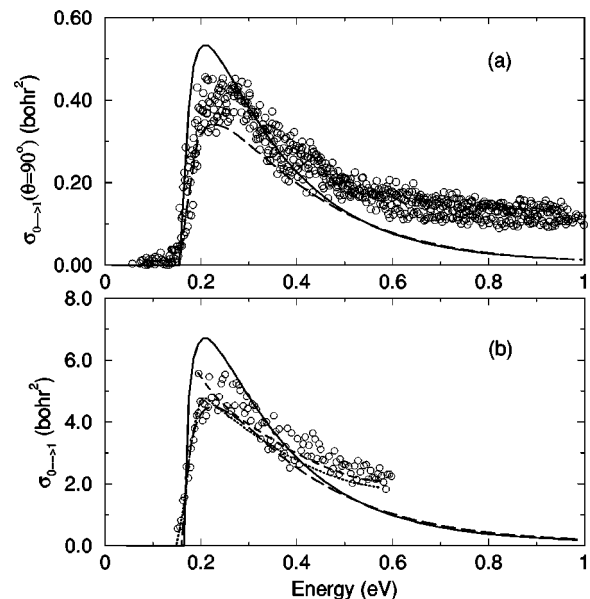

FIG. 2. Vibrationally inelastic (000–100) cross sections for e-CO_2 scattering at energies below 1 eV from the present EMAP+DRP (solid line) and EMAP (long-dash line) calculations. Also shown are the crossed-beam experiment of Kochem *et al.* [11] (open circles). (a) Differential cross sections at 90°; (b) integral cross sections. Also shown in (b) are theoretical results of Morrison and Lane [9] (medium-dash line) and Whitten and Lane [10] (dotted line).
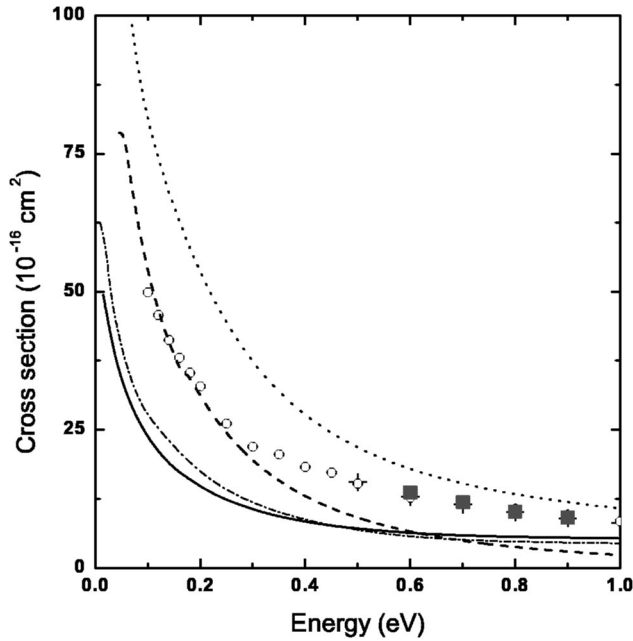
FIG. 3. Vibrationally elastic cross sections for e-CO_2 scattering at energies below 1 eV: present EMAP (solid line) and EMAP with DRP correction (dash line). Also shown are theoretical results of Lee *et al.* [31] (dot-dash line) and Rescigno *et al.* [30] (dot line) and experimental data of Buckman *et al.* [32] (open circles), Ferch *et al.* [7] (pluses), and Szmytkowski and Zubek [35] (solid boxes).

tive to the inner radius of the DRP procedure, which was adjusted to fit the experimental scattering length. Fitting the DRP-corrected Σ_g FN K matrix to a modified effective range theory expansion in powers of k [26,27] for $0 \leq k \leq \kappa$, we find $\kappa = -0.14 a_0^{-1}$ at equilibrium, which corresponds to a scattering length of $A = -7.18 a_0 = -3.80$ Å and to a zero-energy *fixed-nuclei*, elastic cross section of $4\pi A^2 = 647.83 a_0^2 = 181.39$ Å^2. (The vibrationally elastic threshold cross section is known to be about 200 Å [7,13].) Our results confirm that anomalously large values of low-energy cross sections can be attributed to this near-threshold pole of the S matrix.

Figure 1 shows the computed scattering length A and the corresponding pole parameter κ as functions of R_{CO}. The scattering length varies almost linearly, passing through zero at $R_{CO} \approx 2.06 a_0$, near the potential minimum. Data not shown indicate that κ passes through zero near $2.6 a_0$, as in some local-potential models. Thus the physical effect varies smoothly from a virtual state ($A < 0$) for $2.06 a_0 \gtrsim R_{CO} \gtrsim 2.60 a_0$ to weakly bound states outside this range. Although this behavior contrasts with simplified models, our computed cross sections indicate that it describes more realistically the effect of the optical potential that results from correlated wave functions for this polyatomic molecule.

To calculate cross sections via the aforementioned EMAP method, we approximated elements of the vibronic R matrix $R_{vl,v_0,l_0}^\Lambda(\epsilon)$ by vibrational integrals of the corresponding FN R-matrix elements $R_{l,l_0}(\epsilon;R_{CO})$. Diagonal elements ($v = v_0$) are evaluated from $R_{l,l_0}(\epsilon;R_{CO})$ at the appropriate

channel energy $\epsilon = E - E_v$, where E is the total system energy and E_v is the energy of state v. Off-diagonal elements ($v \neq v_0$) are evaluated at the geometric mean of the entrance- and exit-channel energies, $[(E-E_v)(E-E_{v'})]^{1/2}$. The EMAP extension invokes the FN phase matrix [21,28] $\Phi(\epsilon;R_{CO}) \equiv (1/k)\tan^{-1}R(\epsilon;R_{CO})$. Background, justification, and details of these procedures appear in Mazevet *et al.* [22,23,29].

Figure 2 compares EMAP $000 \rightarrow 100$ differential cross sections (DCS) (threshold at 0.1653 eV) to those from crossed-beam experiments of Kochem *et al.* [11]. Part (a) shows their energy dependence at a scattering angle of 90°; part (b) shows $\sigma^{(v)}(000 \rightarrow 100)$ and includes results from previous ANV calculations [9] and from a two-state vibrationally coupled model-potential study [10]. The present *ab initio* cross sections agree very well with the measured data in the vicinity of the near-threshold peak. As the energy increases, $\sigma^{(v)}(000 \rightarrow 100)$ decreases sharply. For the range of onset, Field *et al.* [17] measured 30 meV and for FWHM found 25 meV; by contrast, our values are in close accord with the range 100 meV and FWHM$\approx$200 meV of Kochem *et al.* [11].

There recently appeared two related *ab initio* studies of *vibrationally elastic* e-CO_2 collisions. In the first, Rescigno *et al.* [30] reported total and elastic cross sections based on the complex Kohn method with polarized self-consistent-field functions to represent target polarization. In the second, Lee *et al.* [31] reported elastic cross sections in the FN approximation from Schwinger multichannel calculations using a small set of "polarizing" orbitals. In Fig. 3 integral cross sections from both studies are compared to our uncorrected and DRP-corrected cross sections along with experimental data of Ferch *et al.* [7] and Buckman *et al.* [32]. Our value of the *uncorrected* (equilibrium) scattering length $A = -4.44 a_0$ is consonant with that of Lee *et al.* [31] ($A = -4.51 a_0$); however the DRP correction moves A to $-8.95 a_0$, closer to the swarm-derived value $A = -7.2 a_0$ [25].

The present study illustrates the effect of an s-wave (Σ_g) pole on $\sigma^{(v)}(000 \rightarrow 100)$ near threshold. This mechanism differs fundamentally from vibrational Feshbach resonances that explain analogous peaks in near-threshold cross sections for *polar* molecules [33]. In the vicinity of the peak, our $\sigma^{(v)}(000 \rightarrow 100)$ agree far better with the cross-beam data of Kochem *et al.* [11] than with the synchrotron spectrometer data of Field *et al.* [17], which appear to decrease far too rapidly.

The present research further resolves the long-standing question of whether vibronic nonadiabatic effects participate in near-threshold vibrational peaks [12,21,22,28,34]. From previous e-CO_2 studies [10,12] one might conclude that accurate representation of virtual-state effects requires a nonadiabatic method such as vibrational close coupling or the nonadiabatic phase matrix method [29]. *The EMAP method, however, is fully adiabatic in the near-target region*, where nonadiabatic effects would be most important. This method differs from the conventional ANV approximation in that it

conserves energy and guarantees both unitarity and correct threshold behavior of the most significant elements of the S matrix [23]. We conclude that a proper (adiabatic) treatment of the energetics of the collision—not inclusion of nonadiabatic effects—is required to represent accurately the influence of a virtual-or bound-state pole on near-threshold collisions. This finding should prove useful in future studies of scattering from other nonpolar targets, such as CH_4 and SF_6 [19], whose vibrational cross sections exhibit similar peaks.

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