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Interpretation of the near-threshold behavior of cross sections for e-CO_2 scattering

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Converged coupled-channel calculations of e-CO_2 scattering have been carried out at very low scattering energies. The results are used to show that a virtual state is present in the model static-exchange-polarization e-CO_2 interaction potential used in these calculations. This result provides a possible interpretation for experimental data on total, momentum-transfer, and vibrational-excitation cross sections. A scattering length of $-6.17a_0$ is predicted.

I. INTRODUCTION

The unusual behavior of cross sections for low-energy e-CO_2 collisions has been the subject of attention for several years.[1–5] Experiments indicate that, in spite of the fact that in the $X\,^1\Sigma_g^+$ electronic state CO_2 has zero permanent dipole moment, total and momentum-transfer cross sections for electron scattering from ground-state CO_2 molecules increase sharply as the scattering energy decreases to zero.[3,4] Such behavior is typical of cross sections for electron collisions with polar—rather than nonpolar—targets.[6] This behavior was observed theoretically by Morrison *et al.*[1] in a close-coupling calculation using a model e-CO_2 interaction potential. The formulation of the scattering theory used in this study was predicated on the fixed-nuclei approximation,[7–9] so the vibrational motion of the target was neglected.

In a recent extension of this work based on the adiabatic-nuclear-vibration theory[9,10] Morrison and Lane[2] predicted a sharp threshold structure in the cross section for vibrational excitation of the 100 level of CO_2 —the symmetric stretch mode—from the ground vibrational state. Simultaneous experiments by Wong (private communication) also exhibited this structure. Such peaks have previously been observed[11,12] in vibrational excitation of polar targets, including H_2O, H_2S, HF, HCl, HBr, and CCl_3F. Their presence in these systems has led to a burst of theoretical activity that has continued unabated to the present.[13–23] However, with the exception[24] of CH_4 and perhaps,[25] SF_6, threshold structures are not normally associated with electron scattering from nonpolar targets. Hence their appearance in the excitation of the nonpolar symmetric stretch vibrational mode of CO_2 was somewhat surprising. It is at least clear that a mechanism based on a long-range dipole interaction potential, such as has been proposed to explain the observed threshold peaks in electron-polar collisions,[13–16] cannot play a role in the present e-CO_2 scattering process.

Both the anomalously large low-energy cross sections and the threshold peaks in vibrational-excitation cross sections were produced in theoretical calculations[1,2] that use a model static-exchange-polarization (SEP) potential. The quality of agreement with experiment[4] indicates that this potential is a rather good approximation to the true e-CO_2 interaction, at least for collision energies below ~ 1.0 eV. In the present work, we further explore the properties of this model potential and use it to propose an explanation for the anomalous near-threshold cross sections for the aforementioned e-CO_2 collision processes.

In point of fact, we here present evidence for the existence of a virtual state in the e-CO_2 interaction potential. In Sec. II we briefly review the definition of a virtual state and describe how we isolate the corresponding zero of the s-wave Jost function for this system. Our results are given in Sec. III, which also describes a determination of the scattering length for this system. Comments on the influence of this virtual state on inelastic cross sections are contained in Sec. IV along with a few concluding remarks. Unless otherwise stated, atomic units are used throughout.[26]

II. THEORY: VIRTUAL STATES

Most of the recent flurry of theoretical research on threshold excitation of polar moleucles has

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focused on vibrational excitation of HCl. In a model calculation Dubé and Herzenberg[16] developed a parametrized fit to observed cross sections for this system. Their model attributed the threshold peaks to a virtual-state enhancement of the wave function of the departing electron. Nesbet[17] also discussed the possibility of a virtual state in the e-HCl potential, showing that this mechanism provides a consistent interpretation of existing experimental and theoretical findings for this system. He further showed[17,27] that a virtual state in fixed-nuclei results "implies a separate virtual state associated with each vibrational-excitation threshold," thereby relating the results of fixed-nuclei theory to near-threshold inelastic scattering phenomena.

The conventional picture of a virtual state[28–31] is a nearly-bound state in an attractive potential (with no external barrier). A virtual state is not a "physical state" in the sense of a bound or continuum state with a real energy. Rather, it is a feature of the system, which occurs at a nonphysical energy, that can profoundly influence the scattering cross sections. In potential scattering theory, a virtual state appears as a zero of the s-wave Jost function $f_0(k)$ on the negatiave-imaginary momentum (k) axis or, equivalently, as a pole of the S matrix $s_0 = f_0(-k)/f_0(k)$ on this axis.[32] A virtual-state zero near $k=0$ produces very distinctive behavior in low-energy s-wave cross sections and phase shifts; perhaps the most familiar example is that of scattering from a square-well potential.[30]

If there is a zero of the Jost function at an imaginary momentum near the origin, say at $\bar{k} = i\alpha$, for either $\alpha < 0$ (virtual state) or $\alpha > 0$ (s-wave bound state), then the $l=0$ phase shift $\delta_0(k)$ near $k=0$ behaves as

$$\tan\delta_0(k) = -k/\alpha \ , \tag{1}$$

and the corresponding integrated cross section,

$$\sigma_0(k) = \frac{4\pi}{k^2+\alpha^2} \ , \tag{2}$$

approaches a large finite value at $k=0$. The resulting scattering length, which is defined as

$$A = -\lim_{k\to 0}\frac{1}{k}\tan\delta_0(k) \ , \tag{3}$$

is large. This quantity can be related to the location of the zero by expanding $f_0(k)$ about $\bar{k}$ and retaining only first-order terms, viz.,

$$A = 1/\alpha \ . \tag{4}$$

Thus, we can use $\delta_0(k)$ or, more conveniently, the scattering length A to distinguish a virtual state (A large and *negative*) from a weakly-bound s-wave state (A large and *positive*). Both situations are distinct from an s-wave resonance[28] in which the zero occurs in the lower-half of the k plane near but off the imaginary axis.

The e-CO_2 system is certainly a multichannel problem, being characterized by strong coupling of partial waves.[1,33] However, at very low scattering energies, the cross sections are entirely determined[34] *asymptotically* by contributions from the Σ_g electron-molecule symmetry and, in particular, from the s-wave component of this symmetry. For example, in the fixed-nuclei theory the total cross section is given *at low* k^2 in terms of the body-frame T-matrix elements $T^m_{ll'}$ by[9,35]

$$\sigma = \frac{\pi}{k^2}\sum_{ll'm} |T^m_{ll'}(R)|^2 \simeq \frac{\pi}{k^2}\sum_{\substack{l,l'\\ \text{(even)}}} |T^0_{ll'}(R)|^2$$

$$\simeq \frac{\pi}{k^2}|T^0_{00}(R)|^2 \tag{5}$$

to an excellent approximation. Therefore, we can analyze very-low-energy e-CO_2 collisions by applying the conventional theory of Eqs. (1)–(4) to the $l=0$ eigenphase $\delta_0(\Sigma_g)$.

In general, one can locate a virtual-state pole as $\bar{k} = i\alpha$ by analytically continuing the S matrix into the upper-half k plane[31] and thereby determining α. In the present case, a more convenient procedure is to expand the quantity $k\cot\delta_0(\Sigma_g)$ in a power series[36,37] in k^2 about the location $\bar{k} = i\alpha$ of the zero in $f_0(k)$. To order α^2, this expansion leads to the simple relation

$$k\cot\delta_0(\Sigma_g) = -\alpha + \tfrac{1}{2}\rho k^2 \ , \tag{6}$$

where α and ρ are parameters. The values of these parameters can be calculated from (6) if accurate values of $\delta_0(\Sigma_g)$ are known at two energies.

III. CALCULATIONS AND RESULTS

Since our analysis is based on the equations of Sec. II, we require values of $\delta_0(\Sigma_g)$ at several energies near $k=0$. To determine these eigenphases we extended our previous coupled-channel calculations of e-CO_2 scattering[1] to considerably lower energies. The details of our formulation of the problem have been given previously.[1,33] Briefly, we use the fixed-nuclei approximation in a body-fixed reference frame with the oxygen-carbon internuclear separation fixed at the equilibrium value of 2.194 40 a_0. Scattering channels in each electron-molecule symmetry are therefore simply defined by the (asymptotic) partial-wave order l of the scattering electron.[35] The interaction potential consists of an accurate static potential, a free-electron-gas model-exchange potential, and a semiempirical polarization potential.

To achieve the level of accuracy required for the present study, more stringent convergence criteria were imposed than in our earlier calculations. The Σ_g eigenphases reported here are converged to better than 1.0% in channels. (The number of channels N used at each energy is shown in Table I.) The coupled-channel equations were integrated to a maximum radius of $r=130.0a_0$ for scattering energies from 0.002 to 0.025 Ry. The resulting eigenphases are given in Table I and shown (as dots) in Fig. 1.

It is interesting to note that these results are not consistent with the alternative hypothesis of a low-energy resonance in the Σ_g symmetry. Although highly unusual "s-wave" resonances do exist formally, the phase shifts in such cases display behavior[28] that is quite different from that of Fig. 1. Thus, our Σ_g eigenphases rise from zero but do not display the rapid increase by (approximately) π that would characterize a resonance; indeed, the largest value of $\delta_0(\Sigma_g)$ in Table I is only 0.3777.

One could merely force the data of Table I to fit Eq. (6) (e. g., by a least-squares procedure) and thereby determine values for the parameters α and ρ. However, doing so would not demonstrate that a virtual state is actually present in our e-CO_2 potential. Therefore, we adopt a different procedure.

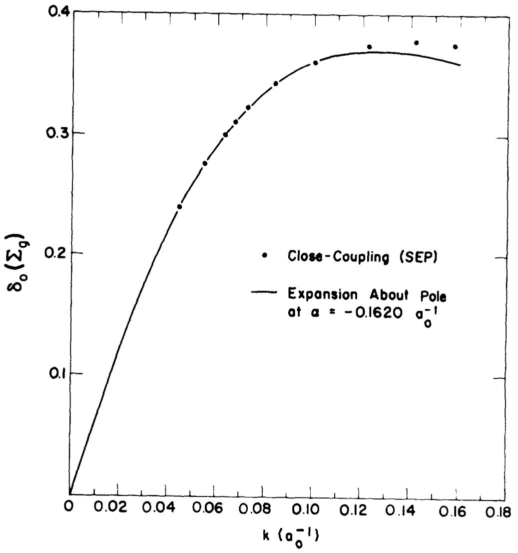

FIG. 1. S-wave eigenphases (modulo π) in the Σ_g symmetry for e-CO_2 scattering as a function of wave number. The dots are the converged coupled-channel results of Table I. The solid curve is calculated by hypothesizing that a virtual-state zero exists at $\alpha=-0.1620a_0^{-1}$.

First, we determine α and ρ by inserting into Eq. (6) s-wave eigenphases at the *two* lowest values of k in Table I— k = 0.045 and 0.055 a_0^{-1}. We obtain $\alpha=-0.1620a_0^{-1}$ and $\rho=20.4380a_0$. Notice that α is negative.

Second, we use these values of α and ρ in Eq. (6) to calculate eigenphases for a range of wave numbers from 0.01 to $0.16a_0^{-1}$, producing the solid curve in Fig. 1. This step amounts to hypothesizing that a virtual-state zero exists at $\bar{k}=i(-0.1620)a_0^{-1}$. To check this hypothesis, we compare the predicted eigenphase sums with the accurate coupled-channel results of Table I, which are shown as dots on Fig. 1.

TABLE I. Converged close-coupling eigenphases (modulo π) for e-CO_2 scattering.

k^2 (Ry)	$k(a_0^{-1})$	$\delta_0(\Sigma_g)$	N[a]
0.002	0.045	0.2404	34
0.003	0.055	0.2770	35
0.004	0.063	0.3000	35
0.0045	0.067	0.3120	36
0.0052	0.072	0.3227	36
0.007	0.084	0.3426	36
0.01	0.100	0.3615	36
0.015	0.123	0.3745	36
0.02	0.141	0.3777	36
0.025	0.158	0.3761	36

[a] Number of channels in close-coupling (SEP) calculations.

The excellent agreement up to $k \sim 0.1a_0^{-1}$ confirms our hypothesis, demonstrating that the coupled-channel results are consistent with Eq. (1) assuming a virtual-state zero of $f_0(k)$ at $\bar{k}=i\alpha$ with $\alpha=-0.1620a_0^{-1}$. The gradual departure of the coupled-channel results from the predictions of Eq. (6) for $k \gtrsim 0.11a_0^{-1}$ is probably due in part to the fact[1] that non-s partial waves [$l,l'>0$ in Eq. (5)] become important for wave numbers above about $0.1a_0^{-1}$.

The corresponding scattering length, from Eq. (4), is $A=-6.17a_0$, and the zero-energy total integrated cross section, from Eq. (2), is $\sigma_{\text{tot}}(k^2=0)=478.83a_0^2$. [An earlier MERT (modified-effective-range-theory) fit[36] to observed momentum-transfer data gave[5] $A=-7.2a_0$.]

IV. CONCLUDING REMARKS

The principal result of the present study is the demonstration that our model e-CO_2 interaction potential supports a virtual state. The agreement between the theoretical cross sections of Morrison *et al.*[1] for scattering energies below a few tenths of an eV and experimental data[3,4] supports the contention that this result offers a likely explanation for the anomalous behavior of the observed low-energy e-CO_2 cross sections. Indeed, the highly suggestive parallel between virtual-state phenomena and the large low-energy cross sections for this system led to the present special effort to isolate the virtual-state zero.

In addition to being consistent with the observed total and momentum-transfer cross sections, the virtual-state mechanism can explain the threshold structure in the 000→100 vibrational excitation cross section. The latter point has been discussed in the context of e-HCl collisions by Nesbet,[17] who showed[27] that a virtual state in a fixed-nuclei calculation will give rise to structures at the thresholds for low-lying vibrational excitations.

In the present case an electron incident on a CO_2 molecule with an energy just above 0.29 eV (the threshold for the 000→100 excitation), leaves with very little kinetic energy after having excited the target. The outgoing electron, which moves in the field of the final state of the target, "feels" the effect of the virtual-state zero, and a sharp peak appears in the corresponding inelastic cross section. Thus the virtual state exerts its influence after the excitation has occurred; this process may be viewed as a final-state interaction.[15,28]

Of course, the quantitative results presented here are only as good as our theoretical model, and refinements of that model are certainly possible, especially in our treatments of exchange and polarization. Nevertheless, we think it unlikely that such refinements would alter the qualitative conclusions of this paper.

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[34] See Fig. 4 of Ref. 1. Conceptually, we use the fact that at low energies the partial-wave coupling disappears as $r \rightarrow \infty$ to replace the e-CO_2 interaction potential by an "effective" spherical potential that reproduces the s-wave eigenphase. Obviously, this procedure is only viable at low energies, when the eigenphase sum in the Σ_g symmetry is totally dominated by a single term that is nearly 100% s wave in character.

[35] The T-matrix elements $T_{l,l'}^{m}$ used here are defined in single-center spherical coordinates as matrix elements of the T operator with respect to the spherical harmonics $Y_l^m(\hat{r})$ and $Y_{l'}^m(\hat{r})$, which form the angular basis function for the theory (see Ref. 1). Thus m labels the symmetry of the electron-molecule system, as $m = 0,1,2,\ldots$ for $\Sigma, \Pi, \Delta.\ldots$

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