

## Enhanced positron annihilation in small gaseous hydrocarbons: Threshold effects from symmetric C-H bond deformations

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The present results report a computational analysis of the effects of symmetric bond stretching during positron scattering from polyatomic hydrocarbon molecules in the gas phase. The collisions are considered at very low energies where the behavior of the  $s$ -wave scattering length can be analyzed and where signatures of virtual state formation appear for all the three systems considered ( $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ ). Furthermore, the present calculations show that the stretching of the CH bonds in all molecules causes the moving of the existing virtual state closer to threshold and further makes it become a bound state whenever highly distorted molecules are involved. The effects of these changes are further seen to cause a marked enhancing of the corresponding annihilation parameters  $Z_{eff}$  at low collision energies, in line with what is experimentally observed for such gases. The significance of such model calculations is discussed in some detail.

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### I. INTRODUCTION

The annihilation of low-energy positrons in atomic and molecular gases is a fundamental process in the field of atomic and molecular physics [1–3]. The experiments and analysis of the data obtained have been conducted for more than four decades, and a large number of atomic and molecular systems have been studied over time, expanding substantially our knowledge of the process and of its dependence on the molecular structures of the medium. On the other hand, in spite of the general progress in the field [4,5], a detailed understanding of the phenomenon has not yet been achieved.

Historically, the quantity of choice for describing the annihilation process has been given through the definition of a dimensionless parameter ( $Z_{eff}$ )

$$Z_{eff} = \frac{\lambda}{\pi r_0^2 c N}, \quad (1)$$

where  $\lambda$  is the observed annihilation rate,  $r_0$  the classical radius of an electron,  $c$  the velocity of light, and  $N$  the atomic and molecular medium number density. The above parameter is a modified version of the original Dirac annihilation rate for a positron impinging on an uncorrelated electron gas [6]. It is therefore regarded as giving the effective number of electrons bound to the target molecule which contribute to the annihilation process. Moreover, the  $Z_{eff}$  values get close to their physical number  $Z = \sum_i Z_i$ , with  $Z_i$  being the atomic numbers of the molecular atoms, for those situations where the Dirac model can be taken as valid. It is also used by us to test the numerical validity of our procedure, as we shall further mention later on.

The accumulated experimental evidence for several atomic and large molecular gases [7,8], however, indicates that the above model is too crude and that  $Z_{eff}$ , which is several orders of magnitude larger than the molecular  $Z$  values, can indeed be found [9]. Various attempts have been made to provide possible explanations for the above findings, from the conjecture that a resonant mechanism may be activated via vibrationally excited molecules [10] to actual calculations of vibrational excitations for the simple diatomic targets [11], to the dynamical formation during vibrational excitations of transient virtual states [12], and to the suggestion of virtual electronic excitations during collisions [13]. On the whole, however, there has been no definitive theoretical evidence—e.g., by solely using *ab initio* calculations for realistic polyatomics, about the microscopic mechanism that should be responsible for the unexpected  $Z_{eff}$  enhancements found in hydrocarbon gases. Recent energy-resolved measurements on smaller hydrocarbons,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  among others, have shown the presence of strong annihilation peaks below vibrational thresholds [14], features which have been related to the possible presence of “core- (vibrationally) excited” Feshbach-type resonances [14]. Further *ab initio* calculations carried out by our group on the collisional cooling of  $CH_4$  and  $C_2H_2$  by slow positrons [12] have indeed shown, for vibrationally excited molecular gases, the presence of virtual-state formation and therefore a marked increase of the scattered positron probability density within the molecular volume, a crucial element for causing  $Z_{eff}$  enhancements.

The role of vibrational degrees of freedom has also been recently explored in a series of model studies [15,16] which attempt to extend the earlier conjecture of the presence of Feshbach resonances [10] to larger networks of vibrational modes by using the densities of vibrational excitation spectra of alkanes [16]. The basic problem with such model studies is that so far we have no computational evidence that the typical interaction between a positron and a polyatomic molecule in its ground electronic-vibrational state would be strong enough to cause the transient target excitations which

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are needed to verify the occurrence of Feshbach resonances [17]. In other words, the basic requirements for a vibrationally mediated Feshbach resonance are that (i) the continuum positron's coupling potentials with the molecular nuclear motion be strong at specific collision energies and (ii) that the  $e^+$ -molecule interaction also provide a "local" energy reservoir that is sufficient to open, "locally" during the scattering process, the molecular vibrationally excited levels which are asymptotically "closed" at the considered collision energies.

In the present study we intend to examine an alternative effect from molecular bond deformations by looking at the threshold behavior of the scattering attributes of positron collisions with  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  when the target molecules undergo marked deformation of their CH-bond stretching modes. We will therefore show first that the present molecules indicate, from the behavior of their  $s$ -wave scattering lengths, the presence of virtual states from near-threshold scattering and then that the molecular structures which correspond to stretched CH bonds of the targets are capable of moving the virtual-state location into the physical, negative-energy region (first Riemann sheet of the complex plane), thereby allowing the possibility of the metastable formation of molecule- $e^+$  compound systems. Since in such transient species a sizable increase of the probability density of the impinging positron over the molecular volume occurs, then we shall discuss below that it causes in turn marked increases of  $Z_{eff}$  values. Although the deformational effects of positrons on molecular gases are still not entirely clear, the present study intends to provide, via the use of realistic quantum calculations, a sort of proof of principle for the possibility that distorted molecular structures in increasingly more complex polyatomics could indeed provide the doorway states to  $Z_{eff}$  enhancement in molecular gases.

The paper is organized as follows: Sec. II briefly reviews our computational model, and Sec. III presents our computational results while our conclusions are summarized in Sec. IV.

## II. COMPUTATIONAL MODEL

Since the details of the present theory have been given before [17–19], we provide the reader only a brief reminder of them. The behavior of low-energy electrons in collisions with atoms and molecules is controlled, in qualitative terms, by the presence of electrostatic interactions with the bound, undistorted target particles, by the attractive exchange interactions with the bound electrons, and by the dynamical electron-electron correlation effects which asymptotically take the simpler form of the dipole polarization forces. As for the positron projectile, on the other hand, the absence of some nonlocal effects such as the electron exchange should make the treatment of its low-energy scattering from many-electron targets less difficult in essence and computationally less demanding in practice. The static potential  $V_{st}$  can be treated exactly, and therefore the way one handles the correlation effects and the long-range (LR) polarization forces, which we shall compound into the positron correlation-polarization potential  $V_{pcp}$ , plays an essential role in the theoretical model.

The present treatment of the short-range part of the full  $V_{pcp}$  interaction was first applied to positron scattering problems by us [19] and is based on constructing the correlation energy  $\varepsilon^{e-p}$  of a localized positron in an electron gas, connecting it with the correct asymptotic form of the spherical dipole polarizability component. The total interaction potential  $V_{tot}$  is therefore the sum of the static interaction between the impinging positron and the (electrons and nuclei) components of the molecular target  $V_{st}$  (for its detailed form see, e.g., Ref. [19]) plus the  $V_{pcp}$  for each geometry  $\mathbf{R}$ :

$$V_{tot}(\mathbf{r}_p|\mathbf{R}) = V_{st}(\mathbf{r}_p|\mathbf{R}) + V_{pcp}(\mathbf{r}_p|\mathbf{R}). \quad (2)$$

The total wave function  $\Psi$  in the molecular body frame (BF) reference system, with the  $z$  axis taken along the direction of the main molecular axis, is expanded around a single center located on the target molecule (SCE):

$$\Psi(\mathbf{r}_1 \cdots \mathbf{r}_Z, \mathbf{r}_p|\mathbf{R}) = \Psi_{mol}(\mathbf{r}_1 \cdots \mathbf{r}_Z|\mathbf{R})\varphi(\mathbf{r}_p|\mathbf{R}), \quad (3)$$

where

$$\varphi(\mathbf{r}_p|\mathbf{R}) = \sum_{l\pi\mu h} r_p^{-1} u_{lh}^{\pi\mu}(r_p|\mathbf{R}) X_{hl}^{\pi\mu}(\hat{\mathbf{r}}_p). \quad (4)$$

In Eq. (3),  $\mathbf{r}_i$  represents the position vector of the  $i$ th electron among the  $Z$  bound electrons in the target, taken from the center of mass. The quantity  $\Psi_{mol}$  represents the electronic wave function for the molecular target. The continuum function  $\varphi(\mathbf{r}_p|\mathbf{R})$  is the wave function of the scattered positron, each  $u_{lh}^{\pi\mu}$  being the radial part of this wave function, and  $X_{hl}^{\pi\mu}$  are the symmetry-adapted angular basis function [18]. The suffix  $\pi$  labels the irreducible representation (IR),  $\mu$  selects a component of the basis if its dimension is greater than 1 and  $h$  does the same within the  $(\pi l)$  set.

If the target molecule can be kept fixed during the collision, we obtain the fixed-nuclei (FN) approximation [18], which ignores the molecular terms of the full Hamiltonian and fixes the value of  $\mathbf{R}$  in each of the target molecules. To solve the Schrödinger equation in the FN approximation, we make use of the BF system rather than the space-frame (SF) reference system, because a formulation in the former can be simpler, both conceptually and computationally. The two frames are related through a frame transformation scheme given, for example, by Refs. [20,21].

After substituting Eq. (4) into the familiar Schrödinger equation of the total system under the FN approximation, we obtain a set of coupled differential equations for  $u_{l\alpha}$  where, for simplicity,  $\alpha$  represents  $(\pi\mu h)$ , collectively,

$$\left\{ \frac{d^2}{dr_p^2} - \frac{l(l+1)}{r_p^2} + k^2 \right\} u_{l\alpha}(r_p|\mathbf{R}) = 2 \sum_{l'\alpha'} \langle l\alpha|V|l'\alpha' \rangle u_{l'\alpha'}(r_p|\mathbf{R}), \quad (5)$$

with

$$\langle l\alpha|V|l'\alpha' \rangle = \int d\hat{\mathbf{r}}_p X_{l\alpha}(\hat{\mathbf{r}}_p)^* V(\mathbf{r}_p|\mathbf{R}) X_{l'\alpha'}(\hat{\mathbf{r}}_p). \quad (6)$$

When solving Eq. (5) under the boundary conditions that the asymptotic form of  $u_{l'\alpha'}$  be represented by a sum containing the incident plane wave of the projectile and the out-

TABLE I. Computational details for the present molecular systems.

Molecule	Basis set	Energy [ $R_{eq}$ ] (hartrees)	$\lambda_{max}^{SCEa}$	$l_{max}^{scatb}$	$r_{max}$ (a.u.) <sup>c</sup>	$(r \times \theta \times \phi)^d$
C <sub>2</sub> H <sub>2</sub>	D95	-76.7992	36	18	146.22	964 × 80 × 148
C <sub>2</sub> H <sub>4</sub>	D95*	-78.0258	28	14	71.28	780 × 64 × 116
C <sub>2</sub> H <sub>6</sub> <sup>e</sup>	D95	-79.2064	28	14	62.96	1000 × 32 × 116

<sup>a</sup>Highest multipolar coefficient of the SCE potential.

<sup>b</sup>Highest contributing partialwave of the scattered position.

<sup>c</sup>Outermost radial integration point.

<sup>d</sup>Total no of points in the polar coordinates of integration.

<sup>e</sup>Staggered configuration.

going spherical wave we obtain the corresponding  $S$ -matrix elements  $S_{l'l'}^{l\alpha}$ . The integral cross section (ICS) is finally obtained from such  $S$ -matrix elements:

$$Q = \frac{\pi}{k^2} \sum_{l\alpha} \sum_{l'\alpha'} |T_{l'l'}^{l\alpha}|^2, \quad (7)$$

where  $T_{l'l'}^{l\alpha} = \delta_{ll'} \delta_{\alpha\alpha'} - S_{l'l'}^{l\alpha}$ . The coupled equation (5) has been solved using Volterra-type integral equations [22].

As mentioned in the Introduction, the  $Z_{eff}$  parameter is a measure, at a given collision energy or for a given temperature of the ambient gas, of the effective number of electrons which take part in the annihilation process. As the collision energy increases, the Born approximation is expected to hold and the positron wave function is approximated by the plane wave of the outer boundary conditions. Hence  $Z_{eff}$  approaches  $Z$ , the number of bound electrons in the molecule, and all the bound molecular electrons are considered as “free” particles [6]. The actual physical situation is, however, different from this simple picture, and therefore  $Z_{eff}$  should be more properly defined as resulting from a multidimensional integration [23,24]:

$$Z_{eff}(k|\mathbf{R}) = \sum_{i=1}^Z \int d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r}_p \delta(\mathbf{r}_i - \mathbf{r}_p) \times |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r}_p|\mathbf{R})|^2. \quad (8)$$

One should note at this point that the form of Eq. (8) implies that the annihilation process we are considering does not involve a permanent electronic excitation after its occurrence. Hence the scattering event includes in our model the distortion of the target electrons during the collision as given by our  $V_{pep}$ . For the present purposes, where we are chiefly interested in *relative* changes, we have not included in Eq. (8) the contributions from modeling enhancement factors [23,24]. The energy-normalized continuum positron wave function obtained from the scattering equation (5) is employed in the overlap integral of Eq. (8) with the electronic wave function of the target molecule, at a given nuclear geometry. The details of the actual numerical calculations have been given before [17] and therefore will not be repeated here. It should also be noted here that when the strength of our  $e^+$ -molecule interaction of Eq. (2) is made to go to zero, then the integral of Eq. (8) correctly yields  $Z_{eff}$

values which coincide with the total number of electrons of the target molecule.

### III. RESULTS FROM PRESENT CALCULATIONS

All calculations have been carried out starting with the Hartree-Fock (HF) description of the occupied molecular orbitals (MO's) of the target molecules, which were initially kept at the nuclear geometries that minimized their total electronic energies. With present-day quantum-chemistry tools one can obviously do much better than that. However, in order to combine *ab initio* methods with model corrections as done in the present study, we limited ourselves to initial HF target states. The various parameters which we have employed when solving the multichannel coupled scattering equations are listed in Table I and provided convergence within 5% for the scattering observables analyzed below. All the bound-state calculations were carried out using the GAUSSIAN 98 package. The terms of the multipolar expansions of the interactions were retained up to the maximum values listed in Table I, where we also report the highest partial waves employed to describe the scattered positron within each of the IR's that contribute to the final cross sections.

In order to initially assess the quality of the model interaction we are using in the present work, we carried out first a set of calculations at the equilibrium geometries for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> and evaluated their corresponding integral elastic (rotationally summed) cross sections in the low-energy regimes, where both experiments [25] and theoretical estimates [26] are available. We have also computed the low-energy behavior of  $Z_{eff}$  for which comparison with earlier calculations [26] was also possible. The results for the cross sections are reported in the two upper panels of Figs. 1 and 2: in the case of acetylene, one clearly sees the very good agreement which is obtained for our calculations with both the experimental values and the earlier calculations. The results for the C<sub>2</sub>H<sub>4</sub> system (upper panel of Fig. 2) are also close to both experiments and earlier calculations in the energy region above 2 eV, while are larger than both in the lower-energy range. The general energy dependence is, however, very similar, although actual cross section values can be larger than existing measurements by almost 100% at the lowest-energy point given by the experiments. The earlier calculations [26] are also larger than experiments at that

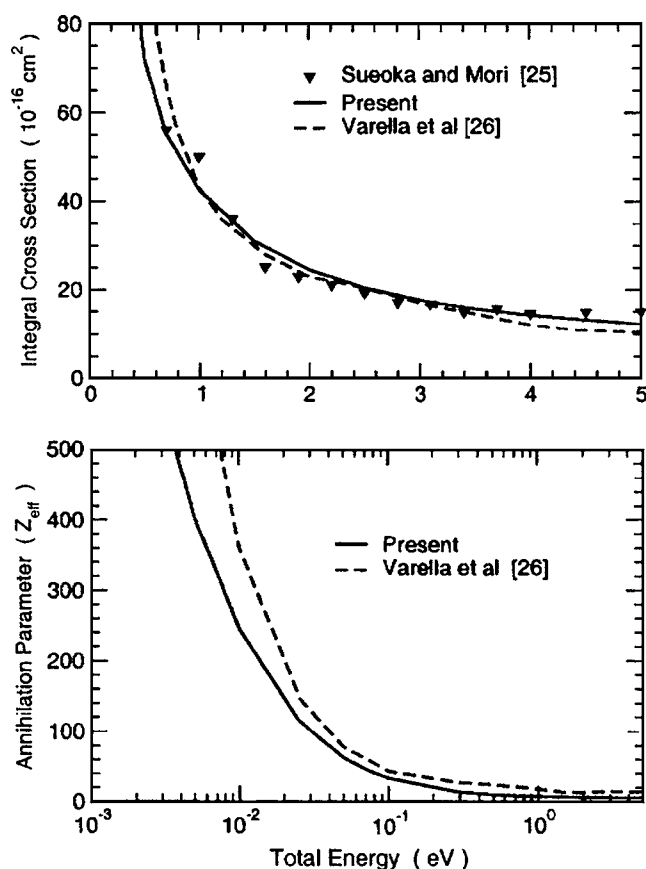


FIG. 1. Computed and measured total cross sections (upper panel) and  $Z_{eff}$  values (lower panel) for the  $C_2H_2$  molecular gas. The experiments are from Ref. [25] and the earlier calculations from Ref. [26].

energy, although still remaining smaller than ours by about 20%.

The  $Z_{eff}$  calculations at the fixed equilibrium geometries are further given by the lower panels of both Figs. 1 and 2, where we sample the energy range below and around 1 eV of collision energy. The earlier calculations of [26] are also reported.

The general energy trends and the orders of magnitude of the calculated  $Z_{eff}$  between our results and the only other existing calculations (which also used a realistic quantum treatment to generate the annihilation parameters [26]) are very similar: only in the very-low-energy regimes of a few meV, in fact, do the two theoretical estimates appear differ, with our methods producing invariably smaller  $Z_{eff}$  near threshold. Since the two theoretical approaches are very different from each other and employ different treatments for both the forces at play and the scattering dynamics, it is not easy to see what might specifically cause the differences in the  $Z_{eff}$  low-energy behavior. On the other hand, given the fact that no other theoretical and computational treatment has been attempted for polyatomic gases by other research groups, we think that it is already somewhat reassuring to see how close the present results are with the outcomes from a totally different theoretical treatment of the annihilation process. We therefore expect that further extensions to the study of vibrational effects may also provide a realistic description of the  $Z_{eff}$  behavior as discussed below.

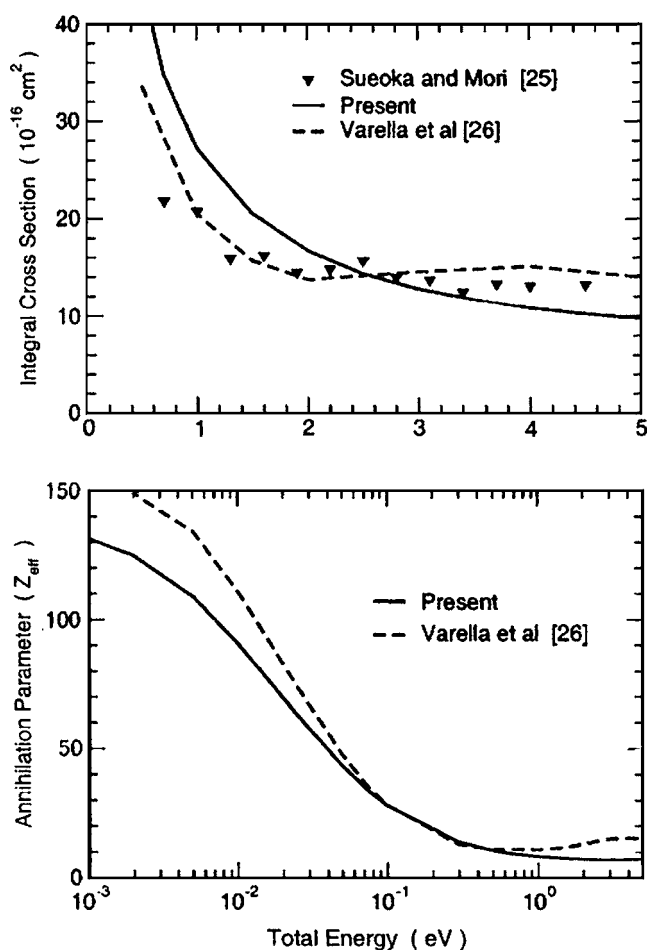


FIG. 2. Same as in Fig. 1 but for the gaseous  $C_2H_4$  molecular target.

The aim of the present study is therefore that of testing whether or not the occurrence of bond stretching deformations of the target molecule, which physically is meant to describe the possible presence of positron-induced transient excitations in the target gas, could be related to the enhancement features in the corresponding  $Z_{eff}$  values observed at room temperature in the sample cells [7–9]. It is interesting to note at this point that recent studies on positron binding to simple diatomics with a variety of methods [27–29] have shown that the optimized structures of the target molecule *after* positron binding can undergo stretching deformations which are up to 40%–50% of the equilibrium value of the isolated molecule. It therefore stands to reason that the transient interaction with a slow, impinging positron at vanishing collision energies could also cause marked bond deformations during the scattering process even though the coupling with the molecular (electrons+nuclei) network remains weak on the whole and not able to actually “open” excited vibrational channels of the target.

To this end, we first performed calculations for the nuclear potential energy curves (PEC’s) associated with the C-H bond-stretching mode and have represented it in an approximate way as solely given by the relative stretching motions of the C and H atoms that preserve the molecular point group symmetry [30].



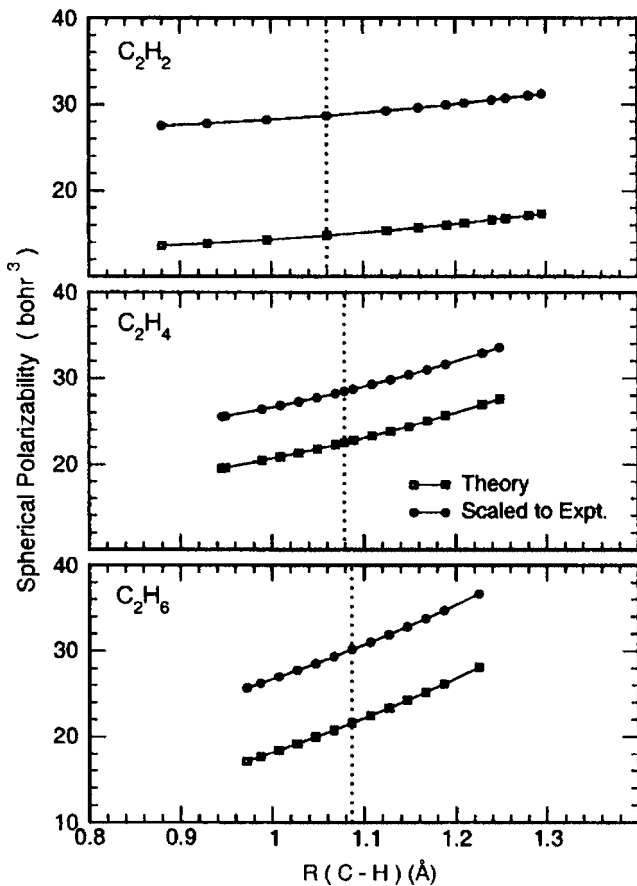


FIG. 3. Computed spherical dipole polarizability values as a function of the  $R_{CH}$  stretching (symmetric mode) in each of the present molecules. Each set of calculation has been scaled to reproduce the experimental values at the equilibrium geometries.

As mentioned earlier, the low-energy behavior of the scattering attributes we shall analyze below is strongly dependent of the LR part of the interaction potential, which is dominated by the dipole polarizability terms. We have therefore computed the spherical polarizability ( $\alpha_0$ ) as a function of the C-H bond ( $R_{CH}$ ) stretching in all the molecules. The results of our calculations are given in the three panels of Fig. 3, where each curve has also been scaled to reproduce the experimental values at the equilibrium geometries. Thus, albeit using a somewhat *ad hoc* procedure, we have empirically obtained what we can consider a realistic description of this quantity as a function of the  $R_{CH}$  coordinates. Since its effects on low-energy scattering attributes is what we have set out to analyze in the present work and given the exploratory nature of the present study, we did not deem it necessary to further extend the quality of the target wave functions in order to produce closer agreement with available polarizability values from experiments. The latter data were, in any event, only available for molecular equilibrium geometries [31].

In order to get a clearer physical picture of the above bond deformation effects on scattering observables very near threshold (as  $k \rightarrow 0$ ), it is useful to remind ourselves of a few characteristic quantities related to that behavior. When the collision energy approaches zero we know that the general

expression of the elastic ICS obtained from a FN calculation at a given  $\mathbf{R}$  geometry is given by [32]

$$Q(k^2; \mathbf{R}) \simeq 4\pi\{A_0(\mathbf{R})\}^2 \quad \text{as } k \rightarrow 0, \quad (9)$$

where  $A_0(\mathbf{R})$  is now the scattering length for the  $s$  wave that is taken to be the dominating component to the ICS at very low energy. It is given as

$$A_0(\mathbf{R}) = -\lim_{k \rightarrow 0} \frac{\tan \eta_0(k; \mathbf{R})}{k}, \quad (10)$$

with  $\eta_0(k; \mathbf{R})$  being the corresponding  $s$ -wave phase shift. We should be reminded at this point that the target molecules are not spherical objects, and therefore the contributing partial waves of the scattered positron are all coupled by the anisotropic interaction. One could, however, define the eigenphases which come from  $S$ -matrix diagonalization and associate the eigenvector coefficients to specific partial-wave contributions [32]: the low-energy dominant term corresponds to the  $l=0$  coefficient. In the presence of a charged partner, as in this case, to describe the effects from the LR polarization forces requires the use of the modified effective-range theory (MERT), which allows us to obtain an explicit expression that links the  $s$ -wave scattering length to the corresponding phase shift [33–36]. Its simplest formulation [32] is as follows:

$$\tan \eta_0(k; \mathbf{R}) = -A_0(\mathbf{R})k \left\{ 1 + \left( \frac{4\alpha_0(\mathbf{R})}{3} \right) k^2 \ln(k) \right\} - \left( \frac{\pi\alpha_0(\mathbf{R})}{3} \right) k^2. \quad (11)$$

The sign of the ensuing scattering length therefore tell us about either the presence of a bound state for the compound system [ $M(\mathbf{R})-e^+$ ] [positive  $A_0(\mathbf{R})$ ] or of the existence of a virtual state for the same complex at negative energies close to the real axis but in the second Riemann sheet [negative  $A_0(\mathbf{R})$ ] [32–37].

The results of the present calculations, carried out by using both Eq. (10) (open circles marked as Xsec) and Eq. (11) (solid lines marked as MERT), are shown in Fig. 4 and are extended down to very low energies of about 1.0 meV. As we clearly see from the three panels of the figure, all three molecules show scattering length values which are negative and therefore our calculations indicate the presence of virtual-state formation within the scattering complexes that contain each of the present molecules. Furthermore, we see that the absolute values of the corresponding  $A_0(\mathbf{R})$  (given as very close to each other by the two methods we employed) decrease from  $C_2H_2$  to  $C_2H_4$  and down to  $C_2H_6$ , which indicates that the energy positions of the corresponding virtual states in the negative-energy region (second sheet) [32],

$$E_0(\mathbf{R}) = -\frac{k^2}{2} \quad \text{with } -ik = \frac{1}{A_0(\mathbf{R})}, \quad (12)$$

get closer to the branch cut on the energy plane as we

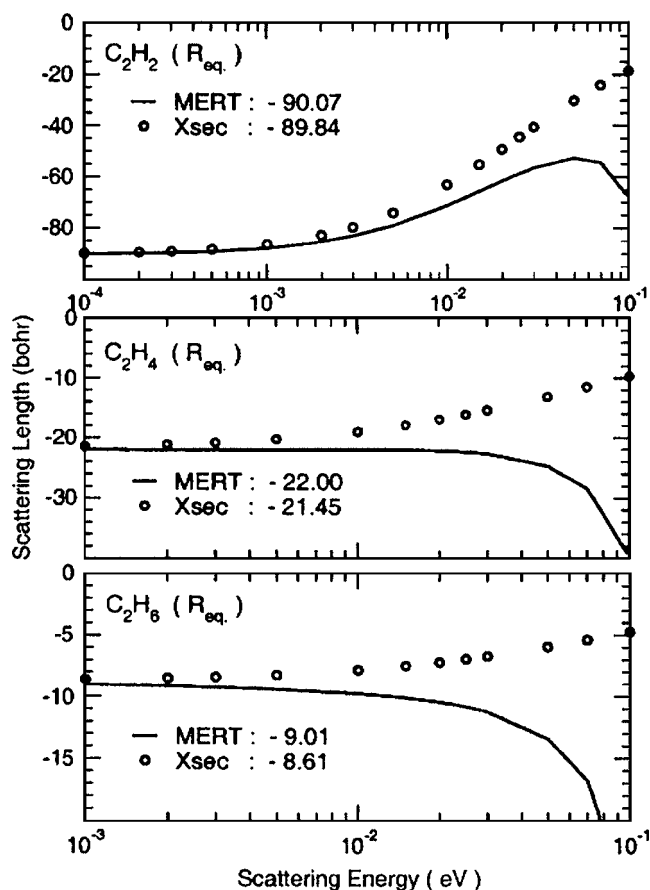


FIG. 4. Computed scattering length for the three molecular systems of this work as a function of collision energies. The solid line is obtained from Eq. (11) of the main text while the open circles are from Eq. (10). The asymptotic values from both calculations are reported in each panel.

progress from  $C_2H_6$  to  $C_2H_2$ , at least from the results of our FN calculations at the molecular equilibrium geometries.

In Fig. 5 we now evaluate the  $A_0$  behavior for all three molecules when we allow the  $R_{CH}$  bond distance to vary over the range reported in that figure. The general features of the scattering length change quite remarkably as we clearly see that all values get closer to the threshold energy axis, show a marked discontinuity, and then cross into the space of positive values when a sufficiently large deformation of the CH bond takes place in each system. In the case of the acetylene molecule, shown in the top panel, we see the divergence occurring for the smallest deformation of the bond—i.e., around  $R_{CH} \sim 1.22 \text{ \AA}$ —after which the scattering length becomes positive and large. This is the signature of the formation of a bound state of the complex  $[M(\mathbf{R})-e^+]$  when the molecule undergoes stretching of its totally symmetric normal coordinate (or of its approximate description by our chosen CH bond deformations). This appearance of a bound state near threshold is an interesting extension, albeit using a simpler computational model, of our earlier results for the same system [12] where correct close-coupling calculations for the vibrational relaxation of a “hot”  $C_2H_2$  ( $n=1$ ) target colliding with a slow positron indicated the formation of a virtual state of the compound system. In the present study,

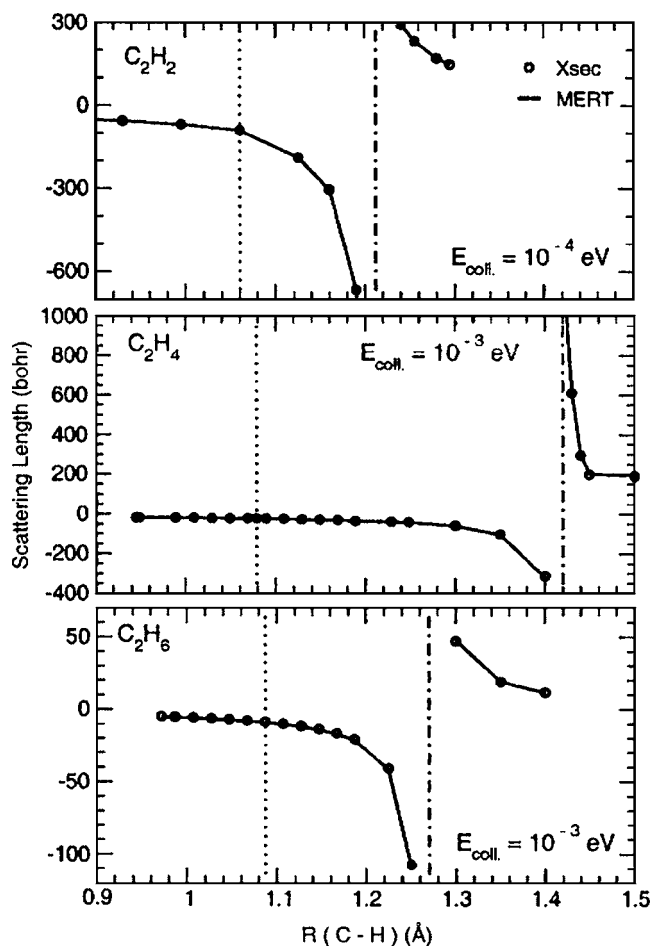


FIG. 5. Computed scattering length for the three molecular systems of this study as a function of the  $R_{CH}$  stretching. The dotted lines indicate their equilibrium values while the dash-dotted lines mark the onset of the critical behaviour of  $A_0(\mathbf{R})$ . The notation is the same as in Fig. 4.

we model the deformation of the molecular targets via the simpler device of stretching one particular bond over a range of values which are going at most up to 30%–40% of their equilibrium values. In other words, we are disregarding for the time being the inclusion of the correct dynamical coupling between impinging positron and nuclear coordinates in the scattering equations and model its effects by simply observing the bond-stretching influence on performing FN calculations for the three title molecules: we further limit the deformation to the same range which has been observed in calculations of optimized geometries of diatomics on  $e^+$  binding [27–29], where finally “stretched” molecular partners were found to be formed on the positron binding process. Thus such deformations are not meant to describe here actual collisions with vibrationally “hot” molecular gases, but rather a transient deformation of the molecule upon interaction with  $e^+$ , where various channels not present in this study (e.g., Ps formation, virtual Ps excitation) could cause the deformation to occur during the scattering interaction times.

An even more transparent presentation of the results is given by Fig. 6, where we report the energy range over

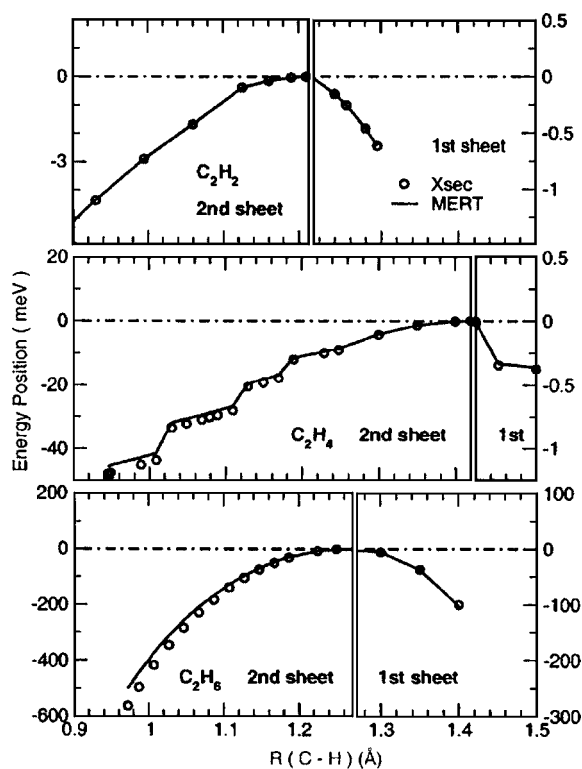


FIG. 6. Computed energy locations of the virtual states for the three molecular systems of this study. The values were obtained using either Eq. (11) (solid lines) or Eq. (10) (open circles) and are given as a function of the  $R_{CH}$  stretching. The first and second Riemann sheets are shown, respectively, on the right and left sides of each panel.

which the virtual states move as the bonds are stretched for all three molecules. The computed energies are given on both the nonphysical (second) and the physical (first) Riemann sheets [32]. Over the range of  $R_{CH}$  values examined in this work we see the following.

(i) The virtual states for the compound systems with  $C_2H_4$  and  $C_2H_6$  cross over into the negative-energy discrete region, but do so only after the molecules reach highly stretched  $R_{CH}$  configurations. The setplike features exhibited by the  $C_2H_4$  calculations (middle panel) are possibly due to numerical artifacts and do not modify the physical picture of the present discussion: by extending our convergence parameters for that molecule, however, the general behavior of the energy trajectory remains the same.

(ii) On the other hand, the  $C_2H_2$  molecule, even when is being stretched by less than 5%, modifies its interaction with the impinging positron strongly enough that the latter could be forming a bound state very close to threshold. This deformation is definitely less than what has been computed for fully bound structures of simpler molecules [38].

The above results therefore suggest that molecular distortion effects which could occur by interaction with very slow positrons are responsible for strengthening the potential between the polyatomic target gases and the impinging slow positron, thereby allowing the latter projectile to occupy a compound state formed during a resonant process involving transient geometry deformations of the molecular partner.

The metastability of such a state could appear (in a more realistic treatment of the dynamical coupling between the molecular nuclear vibrations and the projectile kinetic energy) as a resonance below the energy thresholds for the particular excitation of the corresponding vibrational mode—i.e., as a multichannel virtual state occurring during the transient formation of a deformed molecular target in the presence of the  $e^+$  projectile [12,32,37]. It is interesting to note, as mentioned earlier, that recent quantum-chemical calculations on geometry relaxation effects of molecules as a result of binding with a positron [28,38] found that all of them undergo energy stabilization by marked bond deformation (i.e., bond stretching) on positron attachment.

Another illuminating scattering attribute that could help us to better appreciate the nature of the above processes is given by the evaluation of the time delay, a quantity mostly discussed in the context of resonances [32,39,40] and recently revived when dealing with cold collisions [41] and positron annihilation in atoms [42]. The definition of a time delay through scattering of a given partial wave  $l$  by a potential that goes to zero at least as  $r^{-3}$  is given by [32,39]

$$\Delta t_0(\mathbf{R}) = \frac{2}{k} \frac{d}{dk} \eta_0(k; \mathbf{R}), \quad (13)$$

when considering for simplicity some sort of effective spherical interaction of the projectile with a target molecule of geometry  $\mathbf{R}$ . Making use of the MERT definition of the  $s$ -wave scattering length  $A_0$ , given in Eq. (11), we can also write

$$\Delta t_0(\mathbf{R}) = \frac{-2 \cos^2 \eta_0(k; \mathbf{R})}{k} \left[ A_0(\mathbf{R}) \left\{ 1 + 4\alpha_0(\mathbf{R})k^2 \ln k + \frac{4\alpha_0(\mathbf{R})}{3} k^2 \right\} + \frac{2\pi\alpha_0(\mathbf{R})k}{3} \right], \quad (14)$$

where only the  $l=0$  phase-shift component plays a significant role. Furthermore, one can also follow the Wigner's definition of an isolated resonance [39–41] and examine the behavior of the eigenphase sum at the energy of the virtual state and for each value of  $\mathbf{R}$ , in order to recover a quantity which globally includes the contributions of the higher partial waves to the full scattering dynamics [32].

The calculations shown by Fig. 7 indeed report in the two panels both the behavior of  $\Delta t_0(\mathbf{R})$  as a function of the  $R_{CH}$  stretching (upper panel) and the behavior of the eigenphase sum at the lowest collision energy examined in the present work,  $10^{-4}$  eV, at the energy values where the virtual state for this system was found to reside (lower panel). It is interesting to make the following comments about the present findings.

(i) The positive values of the time delay in the region of molecular geometries where the virtual state exists show an increased slowing down of the positron during the collision which can be delayed up to several ps as the virtual state moves closer to the energy threshold. However, as the compound state becomes a proper bound (metastable) state and the scattering length changes sign (see Fig. 5), we see that the process occurs with a time advance effect since the com-

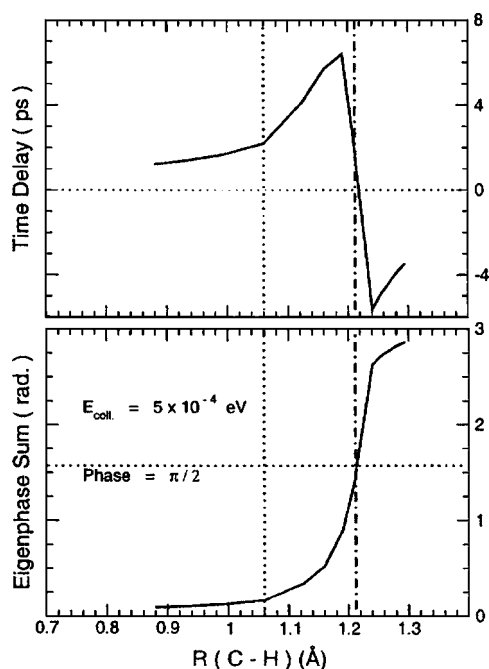


FIG. 7. Computed time delay (units of ps) for the  $C_2H_2$  molecule as a function of  $R_{CH}$  stretching symmetric deformation (upper panel). The lower panel reports the behavior of the eigenphase sums at the lowest energy considered as a function of symmetric bond stretching.

pound state decays much more rapidly. The corresponding positron-to-vibration coupling is therefore becoming stronger and would favor the breakup of the complex by speeding up the whole interaction transfer process.

(ii) The behavior of the eigenphase sum at very low energies, as a function of the  $R_{CH}$  stretching deformation, is also rather illuminating since the lower panel of Fig. 7 shows the presence of a jump by  $\pi$  radians as the molecular geometry is stretched beyond a specific value, thereby indicating the formation of an additional bound state (Levinson's theorem [32]) created by the increased strength of the positron-molecule potential [32]. The appearance of both time and phase discontinuities in Fig. 7 for stretched geometries is indicating, as discussed before, the presence of a zero-energy resonance which can cause such abrupt changes [32].

As mentioned at the beginning, one of the aims of the present work is to link the annihilation parameter large values found experimentally in such systems [9] to our findings of the presence of virtual states and metastable bound states. We therefore carried out the  $Z_{eff}$  calculations at 0.025 eV an energy equivalent to about 300 K.

The  $Z_{eff}$  values for the cases where stretching deformations (symmetric modes) are taken into account are reported in Fig. 8. All the title molecules show a very marked increase of their  $Z_{eff}$  values as the stretching deformation is switched on in the calculations. In each panel the horizontal lines mark the numbers of total electrons ( $Z_N$ ) for each molecule. We see there that, in the case of the  $C_2H_6$  molecule, the  $Z_{eff}$  value increases almost five orders of magnitude when the deformed geometry corresponds to a CH bond which is

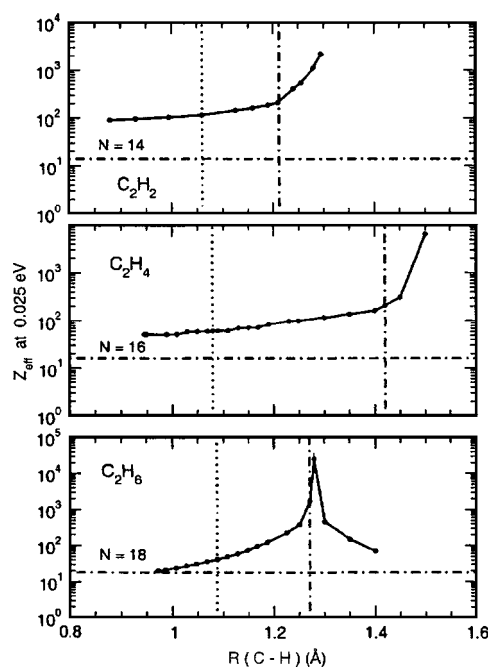


FIG. 8. Computed annihilation parameters for the three molecular systems of this study, reported at the energy equivalent to 300 K, as a function of the  $R_{CH}$  symmetric bond stretching.

about 20% stretched, from its equilibrium value, while for the  $C_2H_4$  target a stronger deformation is needed to achieve marked increases. Finally, in the case of  $C_2H_2$  the interaction potential induced by the CH deformation even relatively smaller bond stretching can cause very marked increases of  $Z_{eff}$  values. This scaling of the stretching-induced effects seems to us to be in qualitative agreement with the experimental findings recently reported for these very molecules [14]. It was shown there, in fact, that in the case of  $C_2H_6$  the resonant peak for the  $Z_{eff}$  increase never went beyond about 1000. Our computed  $Z_{eff}$  increase only requires a local bond deformation during the scattering process of little more than 10% to yield similar  $Z_{eff}$  increases. The experimental data for the  $C_2H_4$  molecule [14] indicate that the energy threshold for the stretching modes does not show a very large  $Z_{eff}$  increase, whereas the bending modes are much more important to yield a large  $Z_{eff}$  value. Our calculations in the middle panel of Fig. 8 indicate that our stretching deformation pulls down the virtual state into a metastable state only for large stretching deformations which could therefore be less likely to occur than the bending deformations in this polyatomic target.

The experiments on acetylene [14] also indicate mild  $Z_{eff}$  increases for the stretching excitation, but rather strong effects from the less energetic bending excitation  $\nu_5$ . Our present calculations, and the earlier ones on the same molecule [43], show the  $C_2H_2$  molecule to be capable of bringing virtual states to become bound (metastable) states when *both* stretching and bending deformations are considered. In our previous calculations [43] we found that the bending deformation is more effective in increasing the  $Z_{eff}$  value and that can bring the annihilation parameter to a range above



TABLE II. Computed  $Z_{eff}$  values at  $E_{coll}=0.025$  eV and as a function of  $R_{CH}$  for  $C_2H_2$  (upper panel) and  $C_2H_4$  (lower panel).

$R$ (Å)	$Z_{eff}$
0.88	90.31
0.93	95.87
0.99	104.49
1.06 ( $R_{eq}$ )	115.49
1.12	144.59
1.16	162.44
1.19	186.41
1.21	209.96
1.24	409.20
1.26	547.83
1.28	1118.10
1.295	2179.9
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0.945	51.905
0.949	51.980
0.989	52.998
1.009	59.364
1.029	60.205
1.049	60.900
1.069	61.527
1.079	61.944
1.089	62.317
1.109	70.364
1.129	71.520
1.149	72.810
1.169	74.099
1.189	84.827
1.229	97.869
1.229	97.869
1.248	99.893
1.300	115.81
1.350	135.57
1.400	161.15
1.420	207.46
1.450	307.72
1.500	6490.3

3000 (as also indicated by the experiments [14]) with only little deformation of the bending motion. Thus it stands to reason to suggest that both types of geometry deformations in  $C_2H_2$  play a role in strengthening its interaction with an impinging positron. One should also mention again at this point that  $Z_{eff}$  values for  $C_2H_2$  and  $C_2H_4$ , which have been computed elsewhere for  $R_{eq}$  values and at the same collision energy we used here [26], indeed are shown to be fairly close to the present findings, as discussed before by us (see Figs. 1 and 2).

In Table II we report the actual values of  $Z_{eff}$  for the  $C_2H_2$  and  $C_2H_4$  molecules as a function of  $R_{CH}$  at a fixed energy of 0.025.

#### IV. CONCLUSIONS

In this work we have analyzed low-energy scattering of positrons from small hydrocarbon molecules with the aim of revealing, from the behavior of scattering observables like scattering length and time delay, a connection between their features as a function of bond-stretching symmetric deformations (involved in the  $\nu_1$  mode excitations of the systems under study) and the experimentally observed enhancements of their corresponding annihilation parameters at room temperature.

The calculations, carried out using nonempirical model interactions, solved the quantum coupled equations over a broad range of molecular geometries pertaining to the C-H bond stretching deformations. In the case of acetylene we have extended here our earlier work on the bending deformation involved in its  $\nu_5$  vibrational mode [43] over the relevant range of molecular geometries in order to model the effects of bond deformation on  $Z_{eff}$  values. The results for the  $C_2H_2$  molecule indicate that both its bond stretching and bending deformations (involved in its  $\nu_1$  and  $\nu_5$  normal modes, respectively) can induce stronger potentials which are able to shift the existing very-low-energy virtual states of the compound system into negative-energy bound states with the target molecule undergoing transient deformation. This is an interesting result which suggests that, if a more realistic dynamical treatment of the vibrational coupling between  $e^+$  and  $C_2H_2$  were to be included, then the corresponding compound states which can be formed during the collision can become metastable to  $e^+$  ejection and their increased local amplitude can cause enhancement of the  $Z_{eff}$  values for that particular molecule.

Our present model, albeit rather simplified in many aspects, thus suggests a connection between the possible existence of metastable compound states (which are formed during transient molecular deformations on positron attachment) and the marked increase of the  $Z_{eff}$  values observed experimentally for these molecules [14]. This deformation effect could then provide a transient molecular mechanism which would in general be active for many polyatomic molecules, but which would certainly become more effective for the larger polyatomic systems where the much higher densities of vibrational states could conceivably produce some form of cooperative enhancement at low collision energies, thus causing  $Z_{eff}$  increases of several orders of magnitude as experimentally observed [14]. This is also reminiscent of the mechanism suggested recently [17] from a modeling of molecular vibrational densities in alkanes, but it differs from it in the sense that we advocate molecular deformations to be the elementary causes for the formation of metastable states which evolve from the initial virtual states that are found to exist in the present series of molecules. Our calculations on the small molecules studied in this work have limited the analysis to only one mode, and even that was described in a simplified form. However, they have shown already that the symmetric stretching modes of their CH bonds are capable of increasing the strength of our modeled  $e^+$  interaction potentials, thereby leading to the evolution of the initial virtual states for the compound system  $M^*-e^+$  into metastable states where the molecular partners undergo a transient relaxation

of their bonds. We are therefore *not* treating the target molecules as physically being vibrationally “hot” targets, a clearly unlikely situation at the temperatures of the experiments [14], but we are saying that  $e^+$ -molecule dynamics can cause large, albeit transient, molecular deformations which enhance the probability density of the positron projectile as  $k \rightarrow 0$  through the existence of virtual states at threshold.

One might also argue, in qualitative terms, that the slow positron will draw electronic charge away from the bonding regions, thereby “weakening” the corresponding vibrational force constants via Ps formation and, further, virtual Ps excitation processes [42].

In conclusion, our calculations have tried to extend the earlier conjecture [10] on the possible existence of vibrationally excited, Feshbach-type resonances in low-energy scattering of positrons from deformed hydrocarbon molecules to the less demanding situation of the existence of virtual-state metastable compounds. For the Feshbach resonance to occur, in fact, one requires stronger interaction potentials between  $e^+$  and the molecules than those obtained thus far from molecular calculations on the systems [12,43–45]. The present model treatment, which initially employs the FN simplification [19], shows that the changes in the  $e^+$ -molecule interaction induced by the nuclear structure deformations of the target molecules are capable of bringing the location of low-lying virtual scattering states onto the physical sheet to become discrete, negative-energy metastable bound states of the  $[M^*-e^+]$  complex. Consequently, it is the marked increase in the probability density of such

states within the physical volume of the target molecular electrons that is causing the increasing of the associated annihilation parameters evaluated at low energy. This result seems in general agreement with what has been experimentally found for a rather broad variety of molecular gases [14] and does not require one to postulate the presence of the more difficult to justify vibrational Feshbach resonances. Although the feasibility of such enhancement mechanisms for smaller systems at room temperature is still not clear, the proof of the existence of such enhancements, as provided by the present study, suggests that their effects in much larger polyatomic targets (which exhibit a much higher density of vibrational channels per unit energy and possibly stronger interactions with the impinging positron) could become proper Feshbach-type resonances and should therefore be taken into consideration when searching for a molecular mechanism which would explain the experiments on the larger hydrocarbons [14].

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