Virtual-State Formation in Positron Scattering from Vibrating Molecules:
A Gateway to Annihilation Enhancement

Tamio Nishimura* and Franco A. Gianturco†

Department of Chemistry and INFM, University of Rome "La Sapienza," Piazzale Aldo Moro 5, 00185 Rome, Italy
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In the present Letter, computational evidence is provided for the first time, choosing the polyatomic CH_4 and C_2H_2 molecules as examples, of the existence of virtual states caused by dynamically coupling molecular vibrations with the positron motion during low-energy scattering processes. Our calculations provide lifetimes longer than vibrational periods, suggesting that the intermediate "compound" configurations could be the gateways through which the rate of annihilation of near-thermal positrons in molecular gases can become orders of magnitude larger than expected from the simpler dynamics, and as it is indeed observed experimentally.

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The behavior of scattering observables in the vicinity of thresholds for atomic and molecular states has been of great interest for a long time and can be studied through the application of limiting laws employed specifically for such energy regions (see, e.g., [1,2]). The features of positron annihilation cross sections (PACSs) observed for very-low energy positrons in molecular gases, on the other hand, have received thus far less attention from theory and computations (for a general discussion, see [3–5] and references therein). The positron scattering from molecular targets also differs considerably from the case of electrons because of the possibility of positronium (Ps) formation and of the resulting annihilation by the emission of two or three γ quanta. For collision systems where the first ionization potential of the target molecule is lower than the Ps binding energy (6.8 eV for its $1s$ ground state), the above reaction is open at all energies, while for the cases where the ionization potential is greater than the binding energy of Ps ($1s$), a variety of other collision processes can still occur below the specific Ps formation threshold.

The positron annihilation rate (λ) in a gas of density n is expressed by the effective number of electrons (Z_{eff}) interacting with one impinging positron as $\lambda = \pi r_0^2 c n Z_{eff}$ [6], where r_0 is the classical electron radius and c is the velocity of light in vacuum. The quantity Z_{eff} can further be given as [3]

$$Z_{eff} = \sum_{i=1}^{N} \int d\mathbf{r}_1, \ldots, d\mathbf{r}_N \, d\mathbf{r}_p \, \delta(\mathbf{r}_i - \mathbf{r}_p)$$
$$\times |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{r}_p)|^2, \qquad (1)$$

where $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{r}_p)$ is the wave function of the total system with the position vectors of the ith molecular electron ($\mathbf{r}_i$) and of the incident positron ($\mathbf{r}_p$) taken from the center of mass (c.m.) of the target. Extensive experimental studies of the above phenomenon have been carried out in recent years [7], and have determined that the annihilation occurs with roughly equal probability on any of the valence electrons [7]. On the other hand, to find the elementary mechanism responsible for the enhanced values of the measured Z_{eff} in larger polyatomic gases, e.g., 142 for methane CH_4 ($N = 10$ where N denotes the number of molecular electrons) and 3160 for acetylene C_2H_2 ($N = 14$) [7] still remains an unsolved problem.

One of the stumbling blocks in providing a quantum mechanical explanation is given by the fact that a molecule provides a "hostile" environment to an incident positron since the screened Coulomb repulsions from the nuclei tend to keep the positron away from its core, cause its local velocity to change little from its asymptotic region, and, generally speaking, reduce the value of the "overlap" integral responsible in Eq. (1) for controlling the size of the Z_{eff} value. A simple model [8] which conjectured the formation of weakly bound e^+-molecule complexes that, by forming vibrationally excited Feshbach-type resonances, would enhance the Z_{eff} values, has not yet been confirmed, at least not for the case of small linear molecules where the actual calculations have been carried out using *ab initio* treatments of the quantum vibrational dynamics [9]. Further recent threshold calculations of vibrationally inelastic cross sections for e^+-CH_4 scattering [10] have also failed to detect the presence of complex formation or of pseudobound states during the excitation/deexcitation processes, and no shape resonances have been detected, or are expected to occur, in the elastic scattering of positrons from polyatomic targets [3]. In spite of the fact that a direct search of such vibration-induced Feshbach resonances for polyatomics of medium or large size with several degrees of freedom still remains outside the range of present day calculations, we intend to show in the present study another possible route to the formation of a temporary complex of [e^+ molecule] at very-low initial kinetic energies (i.e., in the meV range), that are close to those of the experiments [7]. We will show below that the dynamical couplings between the impinging positron and the molecular motion are capable of creating a

marked enhancement of the wave function for the scattered positron, and to have it occur for a time span comparable with the vibrational period of the target molecules considered here, even in situations where no temporary bound states of the complex are found, as would be requested instead for a Feshbach resonance to occur.

The present calculation is based on the fixed nuclear orientation (FNO), i.e., the rotationally sudden approximation, while the vibrational transition is treated within a rigorous close-coupling formulation [11]. Since the rotational periods of the two molecules we consider are of the order of 10^{-12} sec, then the interaction times discussed below are short enough to justify this FNO assumption. We further assume that the target molecule is in its electronically ground state, and we take into account three kinds of interaction (V) between the incident positron and the target molecule: those which originate from an *ab initio* electrostatic potential, the short-range (SR) electron-positron dynamical correlation, and the long-range (LR) target dipole polarization. The target distortion effects in the SR regions are approximated via a parameterfree model potential based on electron-positron correlation in a homogeneous electron gas [12] which is then connected to the LR asymptotic form of the spherical dipole polarization potential [13]. The wave function for the total collision system is expanded as

$$\Psi(\mathbf{r}_p \mid \mathbf{R}) = r_p^{-1} \sum_{l\nu n} u_{l\nu n}(r_p) X_{l\nu}(\hat{\mathbf{r}}_p) \chi_n(\mathbf{R}), \qquad (2)$$

where χ_n is the vibrational wave function of the target with its quantum number n and the variable $\mathbf{R}$ denotes the nuclear geometry. The $u_{l\nu n}$ functions describe the radial parts of the positron wave function and the $X_{l\nu}$ are the symmetry-adapted angular basis functions. The symbol ν globally stands for the indices specifying the irreducible representation of the molecular point groups, and those distinguishing its degenerate members. Then, the quantity $u_{l\nu n}$ satisfies a set of body-fixed vibrational close-coupling (BF-VCC) equations [14],

$$\left\{ \frac{d^2}{dr_p^2} - \frac{l(l+1)}{r_p^2} + k_n^2 \right\} u_{l\nu n}(r_p)$$
$$= 2 \sum_{l'\nu'n'} \langle l\nu n|V|l'\nu'n' \rangle u_{l'\nu'n'}(r_p), \qquad (3)$$

where k_n is written as

$$k_n^2 = 2(E - E_n^{\text{vib}}), \qquad (4)$$

with E_n^{vib} being the energy of the specific molecular vibration. In order to obtain the interaction matrix $\langle l\nu n|V|l'\nu'n' \rangle$ which includes the vibrational channels, we calculate the interaction potential for several molecular geometries, and integrate over such geometries using the relevant vibrational wave functions [14]. By further solving the coupled equations (3), we finally obtain vibrationally elastic and inelastic cross sections.

In the present study, we further restrict our analysis to s-wave scattering as it is the one contribution that dominates at very-low initial kinetic energies ($k_n \to 0$). In the case of the entrance channel being given by the vibrational quantum number n, the total vibrationally elastic and inelastic cross sections are

$$Q_n^{\text{elas}} = \frac{\pi}{k_n^2} |1 - S_{nn}|^2 = 4\pi |a_n|^2, \qquad (5)$$

and

$$Q_n^{\text{inel}} = \frac{\pi}{k_n^2} \sum_{n'(<n)} S_{nn'}^2 = \frac{\pi}{k_n^2} \{1 - |S_{nn}|^2\}, \qquad (6)$$

where $S_{nn'}$ is the element of the scattering S matrix, and $|a_n| = (\alpha_n^2 + \beta_n^2)^{1/2}$, with the real ($\alpha_n$) and imaginary ($\beta_n$) parts of the complex scattering length a_n defined as $a_n = \alpha_n - i\beta_n$ [2]. When one expands the diagonal element S_{nn} in terms of the phase shift, the imaginary part ($\beta_n \geq 0$) is written as [2]

$$\beta_n = \frac{k_n}{4\pi} Q_n^{\text{inel}}. \qquad (7)$$

For the case of the multichannel formulation, one could find, depending on V, an s-wave scattering wave function that corresponds to either a bound or a virtual (unbound) state with its position given by $E_n = -\kappa_n^2/2$ with $\kappa_n = -ik_n = 1/a_n$. The virtual state could then further decay into the asymptotic state of that channel with a lifetime given by

$$\tau_n = \frac{1}{\Gamma_n} = \frac{|a_n|^4}{2|\alpha_n|\beta_n}, \qquad (8)$$

where Γ_n is then a width associated to that process [2].

The target wave functions for CH_4 and C_2H_2 molecules were calculated at the self-consistent field level of accuracy by using our familiar single-center expansion method applied to a multicenter Gaussian-type orbital (GTO) expansion [14]. The basis set was provided by the GAUSSIAN 98 package. We have chosen the D95* GTO basis sets [14] and the terms of the multipolar expansion of the interaction potential were retained up to $l_{0,\text{max}} = 24$ for CH_4 and 36 for C_2H_2. The scattered wave functions of the positron in Eq. (2) were expanded up to $l_{\text{max}} = 12$ and 18 for CH_4 and C_2H_2, respectively, with the inclusion of the lowest three vibrational states $n = 0$, 1, and 2 for the symmetric stretching mode (ν_1), the "breathing" mode examined for both molecules we are discussing here.

We report in Fig. 1 the very-low energy behavior of the elastic (left panel) and inelastic deexcitation (right panel) cross sections for CH_4. The s-wave contributions dominate such cross sections [2] and clearly follow the limiting Wigner's law [1] as $k_n \to 0$ both for the elastic and the deexcitation processes, for all three different vibrational states considered. One can therefore extract from such
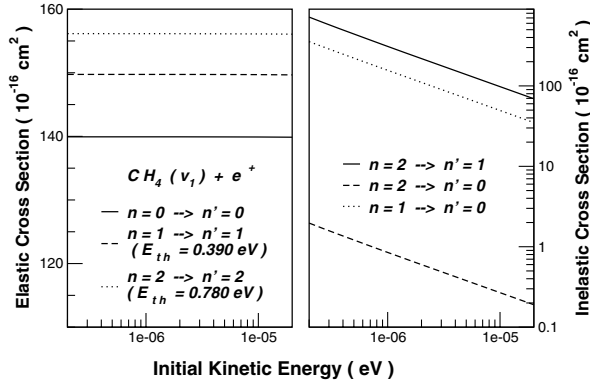
FIG. 1. Vibrationally elastic (left panel) and inelastic (right panel) deexcitation cross sections for the symmetric stretching mode ν_1 of CH_4. See text for details.

FIG. 2. Same as in Fig. 1, but for the C_2H_2 molecule.

quantities the relevant scattering lengths: We report them in the second and third columns of Table I. It is very interesting to see that the real components are all negative, thereby suggesting the existence of low-energy virtual states on the negative branch of the imaginary axis in momentum space. On the other hand, once the coupling with an excited vibrational target is considered and the deexcitation contributions are obtained, the virtual states move away from the imaginary axis and therefore also require real-axis components which describe the decay of such states with a lifetime given by Eq. (8) [15]. The present calculations, reported in the fourth and fifth columns of Table I, clearly show that the virtual states for the excited molecule complexes have now lifetimes that correspond to several vibrations for the normal mode involved [14]. The energy positions of such states can also be found on the physical Riemann's sheet and are located by our calculations (seventh column of Table I) around 300 meV from the zero energy of each vibrationally excited state considered. It is interesting to note here that the energy positions move closer to threshold as the target becomes vibrationally more excited, i.e., as the corresponding interaction potentials become more attractive in the SR region, thereby increasing the capability of supporting a temporary bound state for even stronger interactions. It is therefore possible to conjecture

that for the larger hydrocarbons such increases of potential strength, if they were to occur, may indeed be capable of inducing temporary bound, vibrationally excited $[e^+$-molecule] compounds. They may then become experimentally visible below the threshold of molecular excitation channels as vibrationally induced Feshbach resonances.

Since our calculations show that no bound states exist for the e^+-molecule complex, the s-wave component of the continuum wave function is entirely nodeless at its onset near the origin of our fixed-nuclei reference frame. A typical feature of a virtual state is that of producing scattering wave functions for $l = 0$ which exhibit a larger amplitude within the spatial region of the range of action of the potential [15]. This feature would cause the size of the overlap integrals in Eq. (1) to become larger and to remain so for a fairly long time when compared with the vibrational times of the target molecule.

Another interesting candidate molecule is C_2H_2, where recent experiments [7] have shown a marked increase of the Z_{eff} values when measured at energies below the threshold of the ν_1 mode. Our calculations for the threshold behavior of the s-wave scattering cross sections are reported in Fig. 2, using the same notation of Fig. 1. The size of both the elastic and the inelastic cross sections become very large as each $k_n \to 0$, with the former ones becoming constant, so that the Wigner's law behavior [1] is again confirmed. The values of the $l = 0$ scattering length are shown in Table II, where their real parts indicate the appearance of virtual states which are even closer to threshold than those found in the case of CH_4.

TABLE I. Real and imaginary parts of the scattering length (in a_0), lifetimes (10^{-15} sec) of positron-CH_4 (ν_1: 3147.39 cm^{-1}), vibrational periods (10^{-15} sec), width (meV) of resonance, and the energies of virtual states (meV), as a function of the vibrational level of CH_4 for symmetric stretching mode via the three-state ($n = 0$, 1, and 2) BF-VCC method.

n	α_n	β_n	τ_n	τ_n^{vib}	Γ_n	$|E_n|$
0	-6.3059	0	∞	$\cdots$	0	342.16
1	-6.5233	0.0158	211.95	10.60	3.11	319.73
2	-6.6614	0.0297	120.54	5.30	5.46	306.61

TABLE II. Same as Table I, but for positron C_2H_2 (ν_1: 3603.10 cm^{-1}).

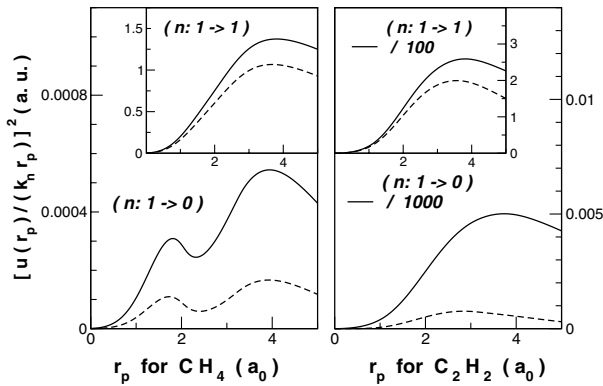| n	α_n	β_n	τ_n	τ_n^{vib}	Γ_n	$|E_n|$
0	-94.917	0	∞	$\cdots$	0	1.510
1	-100.513	1.438	8544.39	9.26	0.077	1.347
2	-100.983	2.306	5407.17	4.63	0.122	1.334

FIG. 3. Squared moduli of the scattering amplitudes for the *s*-wave components of the continuum positron wave function at the virtual state energy value (solid line) and at a scattering energy of 500 meV (dashed line) for CH_4 (left panel) and C_2H_2 (right panel). All quantities are normalized to their energies. The r_p variable represents the distance from the molecular c.m. The solid line values on the two right-side panels are scaled by 10^{-2} (upper) and 10^{-3} (lower), respectively.

The energy positions are around 1 meV (last column of Table II) below the excitation threshold, values which are indeed very close to the location of the Z_{eff} peak experimentally shown by Fig. 13 of Ref. [7] for the same molecule. The corresponding lifetimes are also substantially larger than the vibrational periods (fourth and fifth columns of Table II) and therefore suggest an even stronger influence of the amplitude of this virtual state on the values of the integral in Eq. (1).

An interesting pictorial view of the virtual state effect on the scattering wave function amplitude is reported in Fig. 3. We show there the *s*-wave components for the $(n = 1 \rightarrow n' = 1)$ and $(n = 1 \rightarrow n' = 0)$ scattering amplitudes (energy normalized squared moduli) associated with the virtual states at 319.73 meV for CH_4 and at 1.35 meV for C_2H_2. These data represent the radial parts of the continuum wave functions associated with the scattered positron. The same quantity is also shown for a different scattering energy where no virtual state was found (500 meV). The amplitude variation is seen to be very large for the deexcitation process and suggests that the presence of such states for very-low energy scattering could indeed provide a set of dynamical doorways through which the efficiency of electron-positron direct annihilation gets larger when compared with the values given by the simpler plane-wave Born model [16]. In a larger molecular system, we know that a much higher density of vibrational target states exists within the same range of energies; such "threshold congestion" could therefore further act as a multimode, cooperative enhancement mechanism which might then give rise to the 10^3–10^4 PACSs increases experimentally observed for the larger molecules. Furthermore, the interaction potential modifications induced by such multimode ex-

citations may also be capable of supporting pseudo-bound states below threshold, thereby triggering a Feshbach-type mechanism in the case of the larger systems. Although actual, *ab initio* quantum calculations for such complex systems are still out of present computational capabilities, our study already shows that in the case of the smaller polyatomics the virtual state formation, and its decay (in a multichannel formulation) via vibrational couplings, can indeed provide an enhancement mechanism for the low-energy PACS values which have been observed [7]. Our present conclusions therefore point at an area in which the study of larger polyatomic gases should be undertaken in order to possibly uncover the molecular origins of the observed PACS values. Obviously, the next task is a direct calculation of the Z_{eff} values during vibrationally inelastic collisions. Preliminary results using the adiabatic nuclear vibration approximation [14] for the C_2H_2 stretching mode [3] point at strong vibrational effects for this system.

*Permanent address: 2-11-32, Kawagishi-kami Okaya, Nagano 3940048, Japan.
†Electronic address: fa.gianturco@caspur.it
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