The scattering of positrons from CF₄ molecules at ultralow energies

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Received 25 July 2003
Published 9 December 2003

Abstract
We present a quantum dynamical treatment of the vibrationally elastic scattering off tetrafluorocarbon (CF₄) molecules by very low energy positrons. The present calculation is based on the fixed-nuclei approximation and the interaction potential between the positron and the molecular target includes the \textit{ab initio} electrostatic and the target correlation-polarization effects. The latter contribution is considered by means of a parameter-free model potential based on the density functional theory. The cross sections for this system are obtained by solving multichannel close-coupling equations for the wavefunction of the scattered positron, while no positronium formation channel is taken into account by the present calculation. The elastic cross section, the scattering length ($A₀$) and the location of a virtual state for the total system are obtained and discussed in detail.

1. Introduction
The past several years have witnessed a dramatic increase in studies on very low energy (≈meV) scattering of positrons from atomic and molecular targets (see for example [1, 2] and references therein). This increased activity is partly due to the corresponding improvements on the technology for providing better positron beams to carry out the experiments on molecular targets [3–5].

One of the effects which can be detected in experiments with positrons from atomic and molecular gases is $\mathbf{e}^−\mathbf{e}^+$ annihilation into two or three $\gamma$-rays which can vary between $10^{−10}$ and $10^{−7}$ s. The annihilation rate $\lambda$ for this process is given as [6]

$$\lambda = \pi r_0^2 c N \text{Z}_{\text{eff}}(k),$$

(1)

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where \( r_0 \) is the classical radius of a single electron, \( c \) is the velocity of light in vacuum, \( N \) is the number density of atoms or molecules in the vicinity of the positron projectile, and \( k \) is the associated positron wavenumber. The \( Z_{\text{eff}} \) parameter is a measure, at a given collision energy or at a given temperature of the ambient gas, of the effective number of electrons which take part in the annihilation process when the target interacts with an impinging positron. The \( Z_{\text{eff}} \) parameters measured recently for example for alkanes and alkenes are much larger than the corresponding number of electrons of target molecules by orders of magnitude [5, 7]. On the other hand, the measured value of \( Z_{\text{eff}} \) for the CF\(_4\) molecule is much smaller than that for other fluorocarbons like CH\(_3\)F, CH\(_2\)F\(_2\) or CHF\(_3\) which suggests that the presence of fluorine atoms can reduce the lifetime of the quasi-bound state of the total system (if existing) [5] and the corresponding \( Z_{\text{eff}} \) values to insert into equation (1).

In order to analyse the elementary mechanism at work in the annihilation processes, we have studied low energy positron collisions with diatomic [8] and small polyatomic molecules including CF\(_4\) [9, 10]. In the collision energy region between 0.7 and 9.4 eV for the [CF\(_4\)-e\(^+\)] system where a positronium (Ps) formation channel is closed, we have already succeeded in reproducing the measured total cross sections [11] for the CF\(_4\) gas rather well, by means of parameter-free local model interaction potentials [9, 12]. Furthermore, the conjecture that the enhancements of the \( Z_{\text{eff}} \) values in the very low energy regions (\( \sim \)meV) could be due to the existence of virtual states [13] has been supported by our recent calculations on CH\(_4\) and C\(_2\)H\(_2\) molecules [14].

At such ‘cold’ collision energies, the de Broglie wavelength is very much larger than the spatial size of a target atom or molecule, and its dynamics is dominated by s-wave \((l = 0)\) scattering through the corresponding phaseshift \((\eta_0)\). Therefore, we intend to analyse here in some detail the low energy quantum dynamical treatment of the elastic process for the CF\(_4\) molecule when colliding with very low energy positrons, to our knowledge the first theoretical attempt on this system. The cold energy region is also associated with the \( Z_{\text{eff}} \) parameters [5, 7] observed recently at room temperature, and therefore it would also be interesting to calculate vibrationally elastic cross sections, scattering length and the s-wave phaseshifts at such energies with the intent of analysing in some detail their relations with the behaviour of the experimental \( Z_{\text{eff}} \) parameter [5].

The following section outlines our theoretical approach while section 3 presents our numerical techniques. In section 4, we discuss our results and our conclusions are summarized in section 5. Atomic units (au) are used throughout, unless otherwise stated.

2. The theoretical method

The details of the present theory, which is based on the fixed-nuclei (FN) approximation, have already been reported in our previous papers (see for example [15, 16] and earlier references quoted there). Here, throughout the present calculation, no Ps formation channel (which is supposed to open above 9.40 eV for the CF\(_4\) target) is taken into account. In order to efficiently consider the molecular symmetry, the wavefunction \( \Psi \) of the scattered positron is expanded in terms of the symmetry-adapted angular basis functions \( X^\nu_l \) [17] around the molecular centre of mass,

\[
\Psi(\mathbf{r}) = \frac{1}{r} \sum_{l\nu} f_{l\nu}(r) X^\nu_l (\mathbf{\hat{r}}),
\]

where \( \mathbf{r} \) denotes the position vector of the positron with the origin at the gravity centre of the target. The index \( \nu \) stands for indices collectively specifying an irreducible representation (IR) and those distinguishing the degenerate components with respect to the orbital angular
momentum quantum number $l$ and IR. The above expansion scheme goes under the familiar name of single-centre-expansion (SCE) approach (for example see [1]).

The interaction potential ($V$) between a positron and the target is represented here in the form of a local potential. Then, $V$ is given by the sum of the repulsive electrostatic $V^{\text{el}}$ and the attractive positron correlation-polarization ($V^{\text{pcp}}$) terms. Since cancellation can occur between the two potential terms because of their having opposite signs, this feature makes the resulting cross section values very sensitive to the details of the $V^{\text{pcp}}$ term employed in the calculations. To form $V^{\text{pcp}}$ at short range use is made of a simple parameter-free model potential ($V^{\text{corr}}$).

The fundamental theory to set up the $V^{\text{corr}}$ term is based on an electron–positron correlation energy ($\varepsilon_{\text{e–p}}$) per electron in a homogeneous electron gas. The relationship between $V^{\text{corr}}$ and $\varepsilon_{\text{e–p}}$ is consistent with the local density approximation and a variational principle for a total collision system within the spatial size of the target charges is given by [18]

$$V^{\text{corr}}(r) = \frac{d}{d\rho}[(\rho(r)\varepsilon_{\text{e–p}})[\rho(r)]].$$

where $\rho$ denotes the undistorted electron density of the target. In other words, we assume that the target is always in its ground electronic state. The quantity $\varepsilon_{\text{e–p}}$ was originally derived from an expectation value of the ground state for a Hamiltonian which represents an undistorted electron gas and one positron by Arponen and Pajanne [19]. Based on their work, Boronski and Nieminen [20] have given the interpolation formulae of $\varepsilon_{\text{e–p}}$ over the entire range of the density parameter $r_e$ which satisfies the relationship of $\frac{4}{3}\pi r_e^3\rho(r) = 1$. The above $V^{\text{corr}}$ is then connected with the asymptotic form ($V^{\text{pol}}$)

$$V^{\text{pol}}(r) \underset{r \to \infty}{\sim} -\frac{\alpha_0}{2r^2},$$

at the position of $r = r_e$ (3.10 au in this system) where $V^{\text{corr}}$ and $V^{\text{pol}}$ first cross each other as $r$ increases. Here, $\alpha_0$ is the dipole component of the target spherical polarizability.

In a manner similar to equation (2), the interaction matrix is expanded as

$$\langle l'\nu'|V|l\nu \rangle = \sum_{l'=0}^{l} V_{l'\nu}(r) \int d\tilde{r} X^{l*}_{l'\nu}(\tilde{r})X^{l}_{l\nu}(\tilde{r}).$$

The radial part $f_r$ in equation (2) satisfies a set of coupled differential equations derived from the Schrödinger equation for the total collision system:

$$\left\{ \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + k^2 \right\} f_{l\nu}(r) = 2 \sum_{l'\nu'} \langle l\nu|V|l'\nu' \rangle f_{l'\nu'}(r).$$

By solving these equations, the scattering $S$-matrix is obtained from the asymptotic form of the wavefunction $f_{l\nu}(r)$, and is then used to yield the elastic integral cross sections.

We further restrict our analysis to the $s$-wave ($l = 0$) scattering component that dominates at very low kinetic energies. When making use of the $s$-wave component of the full range of eigenphases obtained from solving equation (6), the scattering length $A_0$ is then given by [21]

$$A_0 \underset{\nu \to 0}{\sim} -\frac{\tan \eta_0(k)}{k}.\quad (7)$$

Furthermore, in the framework of the modified effective range theory (MERT) [22], for scattering whose interaction potential falls off at large distances as $r^{-4}$ (as the polarization potential of equation (4)), the $A_0$ is written as [22, 23]

$$A_0 = -\frac{\tan \eta_0(k) + (\pi \alpha_0/3)k^2}{k[1 + (4\alpha_0/3)k^2 \ln(k)]}.\quad (8)$$
In addition, the energy position of the possible virtual state of the resulting compound system [e−–molecule] is related to the scattering length by the simple relationship (for a detailed discussion, see for example [21] and references therein),

\[ E_{\text{comp}} = -\frac{1}{2(A_0)^2}. \] (9)

Thus, our evaluation of \( A_0 \) from scattering calculations gives also immediately the value of \( E_{\text{comp}} \) of equation (9).

3. Numerical details

The target wavefunction of the electronic ground state for CF₄ was calculated at the self-consistent field level using our familiar single-centre expansion (SCE method [16]) applied to a multicentre Gaussian-type orbital (GTO) expansion, and the basis set employed was provided by the Gaussian 98 package [24]. The GTO basis sets we have chosen are those of D95* type which consist of (9s5p1d)/[4s2p1d] for C and F atoms which is the same as that employed in our recent calculation on positron scattering [9]. The terms of the multipolar expansion of the interaction potential in equation (5) were retained up to \( l_0 = 100 \), and the scattered wavefunction of the electron in equation (6) was expanded up to \( l = 50 \) which yielded the obtained cross sections converged to within 0.1% (see figure 1). For the specific information of all the required parameters and properties which we study in the present work, see tables 1 and 2. In order to solve the close-coupling equations by means of standard Green function techniques, equation (6) is rewritten as an integral equation (a Volterra equation: for details, see [25, 26]). For the asymptotic part of the \( V^{\text{PS}} \), i.e. \( V^{\text{pol}} \), we first obtained the value of
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Table 1. Molecular properties of CF₄ at the equilibrium geometry.

<table>
<thead>
<tr>
<th>C–F (Å)</th>
<th>GTO basis sets</th>
<th>( E_{\text{SCF}} ) (au)</th>
<th>( \alpha_0 ) (au)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3187</td>
<td>D95*: (9s5p1d)/[4s2p1d] for C and F atoms</td>
<td>−435.765 37</td>
<td>19.60</td>
</tr>
</tbody>
</table>

\(^a\) Spherical dipole polarizability.

Table 2. Computational details of the CF₄–e\(^+\) system.

<table>
<thead>
<tr>
<th>( l_{\text{max}} )(^a)</th>
<th>( l_{\text{max}} )(^b)</th>
<th>Maximum number of coupled channels</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>50</td>
<td>100, 121, A₂ = 96, E = 217, ( T_1 ) = 312, ( T_2 ) = 338</td>
</tr>
</tbody>
</table>

\(^a\) Maximum parameter of the potential expansion.
\(^b\) Maximum parameter for the partial wave expansion of the continuum positron.

\( \alpha_0 \) from the target wavefunction with the GTO basis set of D95* employed, and then we normalized its results to the experimental value of \( \alpha_0 \) for the molecular equilibrium geometry (see table 1).

It is also interesting to note that recent work on atomic systems and model potentials [27, 28] has developed very interesting relations between the computed scattering length and the behaviour of \( Z_{\text{eff}} \) at low energies. These relations will not, however, be discussed in the present work and will be the object of a separate study carried out in our group [29].

4. Results and discussion

In the upper panel of figure 1 we report the contribution from the \( A_1 \) IR to the total elastic (rotationally summed) cross sections in the region of very low collision energies. The various curves reported show the level of numerical convergence reached with two crucial expansion parameters: \( \lambda_{\text{max}} \), the multipolar expansion index for the \( V_{\text{pcp}} \) potential, and \( l_{\text{max}} \), the partial wave expansion index for the scattered positron projectile. The former parameter labels the quality of the description of the computed static multipoles from the target electronuclear network, while the latter describes the convergence of the close-coupled dynamical equations. We clearly see from the figure that the filled-in circles correspond to the parameters chosen which yield well converged cross section values down to the Ramsauer–Townsend minimum (RTM) feature shown by the \( A_1 \) IR contribution.

The lower panel of the same figure shows the convergence study carried out for the \( T_2 \) contribution to the total elastic cross section: only one of the three components is shown in the figure. We see again that the filled-in circles describe well the converged values of that component of the cross section, reaching convergence much more rapidly than in the case of the RTM region in the upper panel. In both instances we need rather large \( \lambda_{\text{max}} \) values to realistically describe the OCE expansion of the full interaction.

Since we are interested in ensuring converged cross sections down to ultralow collision energies, so that the corresponding scattering length values could be reliably obtained, we report in figure 2 some of our numerical tests carried out for this purpose.

The upper panel of that figure shows the calculated phaseshifts obtained from the full calculations as a function of the number of partial waves included in each calculation: \( l_{\text{max}} \) values up to 25\( \hbar \) have been included and we see that the total phaseshift has essentially converged for \( l_{\text{max}} \) values around about 15\( \hbar \). We also see that, at the considered energy of \( 10^{-5} \) eV, the total phaseshift is essentially given by its s-wave component, as expected.

The lower panel of the same figure reports the partial cross section computed at the same ultralow energy as a function of the partial wave expansion: here again we see that converged
values are obtained by the time $l_{\text{max}}$ becomes about $15\hbar$ and that the dominant contribution to the total elastic cross section remains the s-wave contribution of the $A_1$ IR component.

One should understand here that we are discussing the numerical convergence with our present model potential. Hence, the physical reliability of the final results should be judged in a direct comparison with existing experiments. We have already done so for the CF$_4$ target gas using the experiments carried out at higher collision energies [9] and found there good accord between our calculations and the experiments. By inference, therefore, we also expect our low energy calculations to be fairly realistic when describing that physical process, provided their numerical convergence is reached as shown in the present work.

Having been satisfied with the converged tests of the calculations, we then computed the corresponding scattering length values using both formulae discussed in the previous section: the scattering length $A_0$ from equation (7), labelled as ‘Xsec’ in our figure 3, and the $A_0$ from equation (8), labelled as ‘MERT’ in our figure 3.

In the two panels of that figure we report the behaviour of the two sets of calculations. In the panel on the right we show calculations at the relatively high energy between 90 and 30 meV. The two approaches yield both negative $A_0$ values but still are very different from each other, indicating that the asymptotic behaviour at vanishing collision energy has not yet been reached and that the two methods converge with very different rates.

On the other hand, the left panel reports the same set of calculations for $A_0$ but carried out down to $10^{-5}$ eV: we see there that both methods now essentially yield similar values that differ from each other by less than 1%. Both calculations give for this system negative values of the $l = 0$ scattering length, thus suggesting the presence of a virtual state for the [CH$_4$–e$^+$] compound system. However, the value found for $A_0$ is a small one since it corresponds to less than 2.0 au. It follows that the corresponding energy (on the second Riemann sheet) as given
via equation (9) in the present calculations and shown in figure 3 corresponds to about 4 eV, i.e. to a very unusual ‘virtual’ state located very far away from the branch cut and way down on the negative energy axis.

This result indicates that the CF₄ molecule can give rise to something similar to a conventional ‘virtual’ state but that such a state is now located so deep down on the negative energy axis and away from the energy threshold to have a limited effect on the scattering attributes of the present system. In our earlier analysis of such features from scattering length calculations of other polyatomic gases interacting with slow positron beams [14, 27], we had found that the existing negative scattering length values yielded virtual states which, as usually expected [21], were positioned only a few millielectronvolts below the energy threshold and therefore the relevant scattering wavefunction for the positron partner acquired the features of a zero energy resonance [21]. This feature meant that its scattered wavefunction s-wave amplitude within the physical size of the target molecule became much larger and therefore could provide $Z_{\text{eff}}$ values at those energies (close to 0.025 eV) markedly larger with respect to the values given by the simple sum of atomic numbers of the component atoms. In other words, the existence of virtual states near the energy thresholds were taken as indicators of the possible existence of ‘nascent’ bound states on the physical Riemann sheet that could then be reached in the presence of transient molecular excitations into higher vibrational states. Such processes due to the modified e⁺–molecule interaction could then provide a microscopic mechanism for the formation of metastable states through Feshbach-type resonances [21, 13] and thus an explanation for the marked $Z_{\text{eff}}$ enhancements experimentally observed in large systems [13, 7].

In the present case, however, we find that the virtual state ‘signature’, i.e. the negative value of the scattering length, is a rather small value which yields a negative energy located very far from the threshold of the elastic scattering process we are considering. If one further
notes that the experimental data for CF$_4$ [5] do not exhibit any marked $Z_{\text{eff}}$ enhancement with respect to the simple $Z = \sum_i Z_i$ of the component atoms, then it stands to reason to relate such a diversity of annihilation efficiency with the diversity of the features of the virtual state found by the present calculations. Thus, the fact that the CF$_4$ molecule is found, at odds with the behaviour of other polyatomics [30], to exhibit a virtual state well away from the zero energy axis, can be used to explain why it also exhibits very small $Z_{\text{eff}}$ values at room temperature. This means that if one can connect the behaviour of the molecular annihilation parameters with the scattering observables at ultralow collision energies, a valid operation for a theoretical analysis [27, 28], one finds that this title molecule lacks scattering amplitude enhancement because of its not having a zero energy resonance [21].

5. Summary and present conclusions

In this work we have analysed in some detail the scattering behaviour of positron collisions with CF$_4$ molecules at ultralow energies, keeping the molecule at its equilibrium geometry. The calculations show the presence of an RTM feature at low energies, the existence of a small, negative scattering length value and the lack of $e^+$ bound states with the title molecule.

The location of that virtual state was found to be quite far from the zero energy threshold and certainly further away from it than any of the previously computed virtual states for polyatomic targets [14, 30]. The fact that the CF$_4$ molecule does not show in the experiments any annihilation parameter enhancement [5], as seen instead in other hydrocarbon molecules, is therefore taken as a confirmation of the fact that such enhancement effects can be induced by the presence of virtual states of the compound systems (M–$e^+$) located on the non-physical Riemann sheet and very close to the zero energy position. This means that, in those situations, the possible presence of molecular vibrationally excited states could induce a strong enough perturbation of the positron–molecule interaction as to bring that virtual state onto the physical sheet, thereby making it a metastable bound state that would enhance the annihilation process by increasing the overlap between the bound electrons and the scattered positron wavefunctions [13, 14, 30] and thus giving rise to a Feshbach-type transient compound state. Such a possibility, however, should not exist during the $e^-–$CF$_4$ annihilation processes since the location of a virtual state is found to be far from the energy threshold and would require too strong a perturbation of the interaction for it to be able to move such a state into becoming a metastable bound state with a vibrationally excited CF$_4$ molecule. Hence, the lack of experimental evidence at room temperature of any $Z_{\text{eff}}$ enhancement feature for the title molecule can be linked to the special features of the scattering length found by the present calculations. In physical terms, however, we also invoke the special electronic properties of the fluorine atoms and the particular ‘hardness’ of their interactions within the molecule that would defy any strong perturbation caused by the incoming positron.

Acknowledgments

The financial support of the Research Committee of the University of Rome ‘La Sapienza’ (URLS), of the Ministry for University and Research (MUIR) and of the CASPUR supercomputing centre is gratefully acknowledged. This work was also part of the European network EPIC, of which URLS is one of the Research nodes. Finally, one of us (TN) thanks the CASPUR Supercomputing Centre for the awarding of a Research Fellowship.
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References