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Electron Induced Processing
at the Molecular Level (EIPAM)

Vibrational-Inelastic Positron-Scattering off Acetylene

and

Writing of a Review Article on Positron-Molecule Interactions

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Purpose of the visit

The purpose of the visit in the group of Prof. Gianturco at the University of Rome *La Sapienza* was to carry out calculations on vibrational-inelastic positron-scattering off acetylene (C_2H_2) and to initiate the writing of a review article on positron-molecule interactions.

We have decided to extend the proposed research program and to start with a study of electron- and positron-excitation of the strongly dipole-allowed antisymmetric stretching (ν_3) mode of tetrafluoro-methane (CF_4), because of the availability of experimental measurements [1, 2, 3, 4]. This study provided a good assessment of our underlying physical model and a challenging test for our numerical methods.

Work carried out

In our calculations of vibrational-inelastic scattering we are solving the body-fixed vibrational close-coupling equations (BF-VCC) (for more details see e.g. [7]). We are using the single-center-expansion method using asymptotically corrected model potentials derived from density functional theory (for more details see e.g. [6, 5]).

We have started our investigation with detailed convergence tests on the two dipole-allowed vibrational modes of CF_4, the antisymmetric stretching (ν_3) and the antisymmetric bending (ν_4) mode. They are depicted in figures 1 and 2, respectively. The relative amplitude of the nuclei within the normal modes is visualized by arrows.

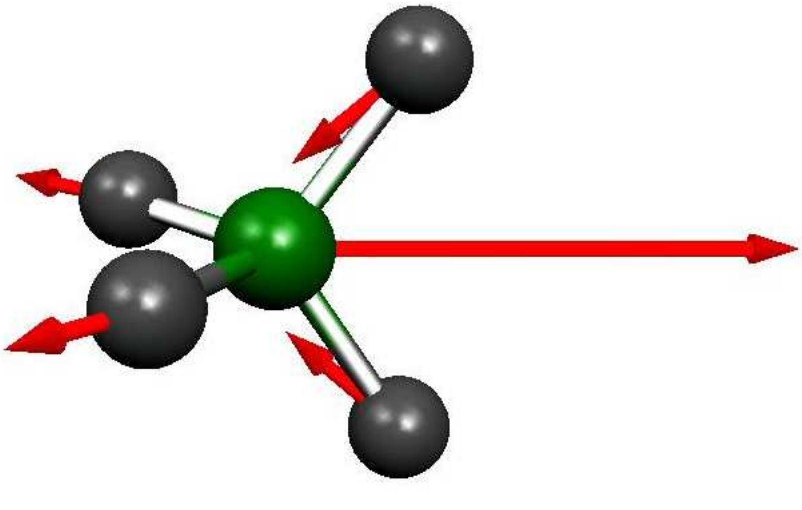

Figure 1: Pictorial representation of the antisymmetric stretching (ν_3) vibrational normal mode in CF_4. Only one of the three degenerated components is shown.

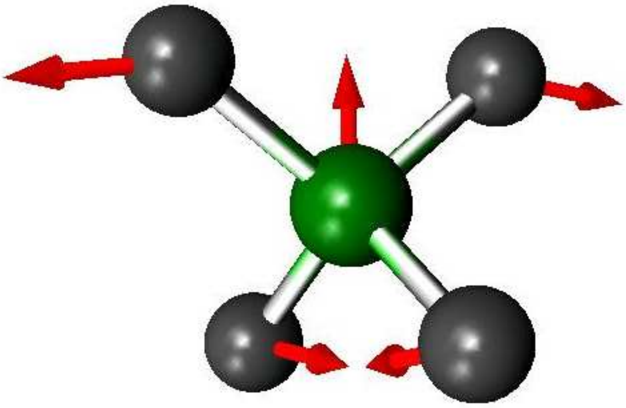

Figure 2: Pictorial representation of the antisymmetric bending (ν_4) vibrational normal mode in CF_4. Only one of the three degenerated components is shown.

From the arrows in the figures one can notice that the central carbon atom is fulfilling a large amplitude motion in the v_3 mode. In the v_4 mode all atoms are moving by nearly the same amplitude. This behaviour is in some contrast to molecules like H_2O and CH_4, which have been studied previously with the BF-VCC method [7, 8]. In these molecules the heavy nucleus is doing only small movements during the vibrations, whereas the hydrogen atoms are vibrating with large amplitudes, due to their smaller nuclear mass. This different character of the normal modes of CF_4 is slowing down the convergence of numerical integration that for generating the vibrational close-coupling (VCC) potential. A matrix element of the VCC-potential that couples two different vibrational energy levels n and n' of the vibrational mode ν_i is given by

$$\langle n|V_{l_0m_0}|n'\rangle_{\nu_i} = \int d\mathbf{R}\ \chi_n^{\nu_i}(\mathbf{R})\ V_{l_0m_0}(r_p|\mathbf{R})\ \chi_{n'}^{\nu_i}(\mathbf{R})\ . \tag{1}$$

Here $V_{l_0m_0}(r_p|\mathbf{R})$ is one (l_0m_0)-component of the single-center expanded potential at the nuclear geometry $\mathbf{R}$, $\chi_n^{\nu_i}(\mathbf{R})$ is the vibrational wavefunction, and r_p is the distance of the colliding particle (electron or positron) from the scattering center.

A higher accuracy of the integration could be achieved by increasing the number of grid-points, a better description of the vibrational wavefunction and a higher accuracy in the representation of the vibrational normal coordinates. In order to get more accurate normal coordinates and to have a better control of the chosen Abelian subgroup, we decided use the Quantum Chemistry program package TURBOMOLE [9] instead of the previously used GAUSSIAN program package [10]. This required the implementation of a new interface between TURBOMOLE and the VOLVCC suite of programs, that performs the BF-VCC calculations.

Some results for excitating the two dipole-allowed vibrational modes CF_4 by positron and electron impact are presented in the next session. These calculations are including polarization and correlation effects between the target molecule and the impinging particle. In order to get a better understanding of the underlying physical effects and differences between positron and electron impact, we have performed calculations in which we have switched off the polarization and correlation.

With our improved tools we have set up calculations for the vibrational modes of C_2H_2. The computations are still in work. Furthermore we are also working on simulations of the excitation of the two dipole-forbidden vibrational modes of CF_4.

We have started the writing of the review article on positron-molecule interactions. This work is still ongoing.

Main results

In figure 3 and 4 we are presenting computed cross sections for the excitation from the vibrational ground state into the first excited state of the dipole allowed vibrational modes of CF_4 by electron and positron impact.

Figure 3 is showing calculated and experimental cross sections for the excitation of the antisymmetric stretching (ν_3) vibrational mode. Also shown are recent experiments results by Marler and Surko [1]. In our calculations the scattering wavefunction was expanded up to l_{max} values of 12,18 and 24. The potential was expanded up to $l_{0,max} = 24, 36,$ and 48, respectively. Both, calculated electron and positron cross sections, are converged for $l_{max} = 18$ and $l_{0,max} = 36$. Near threshold the calculated positron cross section is approximately 50 per cent higher than the corresponding cross section for electron impact. For higher energies this difference becomes smaller. The experimental cross sections for electron and positron impact are both of comparable size. Directly above threshold the experimental cross sections are close to our calculated values for electron impact. Towards higher energies the experimental cross section is decreasing much slower than our computed results.

Figure 4 is showing our calculated excitation cross sections for the antisymmetric bending (ν_4) vibrational mode for positron and electron impact. The scattering wavefunction was expanded up to l_{max} values of 12, and 18. The potential was expanded up to $l_{0,max}$ = 24, and 36, respectively. The computed cross sections are decreasing by 60 per cent, if the the expansion of the scattering wavefunction is increased from $l_{max} = 12$ to $l_{max} = 18$, and the representation of the potential is increased from $l_{0,max} = 24$ to $l_{0,max} = 36$. Here more convergence tests will be necessary. As for the antisymmetric stretching mode, the excitation cross section for the antisymmetric bending mode his approximately 50 per cent higher for positron impact than for electron impact. The maximum of the cross

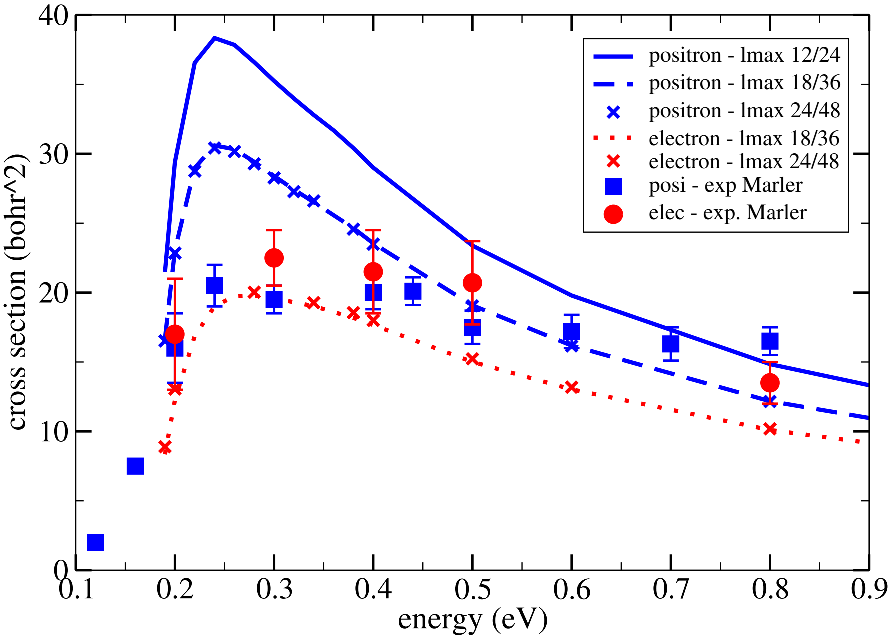

Figure 3: cross sections for the excitation out of the vibrational ground state into the first excited state of the antisymmetric stretching (ν_3) mode in CF_4 by positron and electron impact. The experimental data is taken from Marler and Surko [1].

sections for exciting the antisymmetric bending mode is about five times smaller than the maximum of the cross section for exciting the antisymmetric stretching mode. Calculutions using the Born-dipole approximation are suggesting a factor of about 20 for the same quantity [3, 4].

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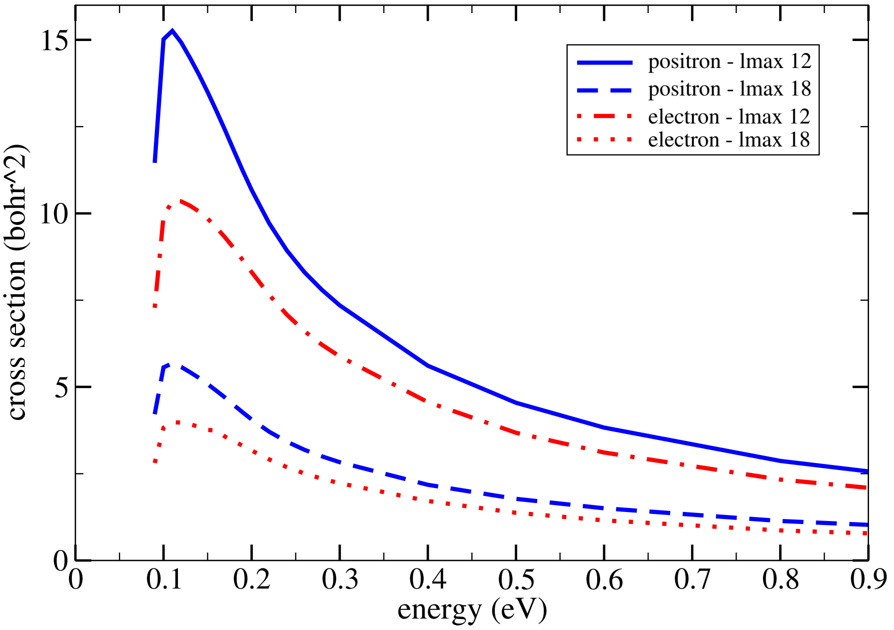

Figure 4: cross sections for the excitation out of the vibrational ground state into the first excited state the antisymmetric bending (ν_4) mode in CF_4 by positron and electron impact.

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Future collaboration with host insitution

We will continue collaboration on vibrational-inelastic electron and positron scattering off CF_4, and C_2H_2 molecules. Furthermore joint work on the review article on positron-molecule interactions is ongoing.

Projected publications resulting from the grant

It is envisaged to publish the results on vibrational inelastic electron and positron scattering off CF_4 later this year. Calculations on vibrational inelastic electron and positron scattering off C_2H_2 are still carried out and will result in further publications.

Work on a review article on positron-molecule interactions is result in another publication.

Other comments

We acknowledge computer time, which has been made available by the CASPUR computer consortium (Rome, Italy) and by Prof. S.D. Peyerimhoff (University of Bonn, Germany). Furthermore we acknowledge discussions with Dr. F. Furche (University of Karlsruhe, Germany) about TURBOMOLE which helped us in the implementation of an interface between the TURBOMOLE program package and the VOLVCC suite of programs for solving the vibrational close coupling equations.