

Purpose of the visit

Recently the Prague group extended¹ the computational method called DMR (Discrete Momentum Representation) to calculation of cross sections for vibrationally inelastic electron scattering by polyatomic molecules.

In IR spectroscopy non-zero change of dipole moment leads to rise of IR intensity for the particular vibrational mode. In electron-molecule collisions similar trends can be observed in near forward scattering but the correlation between electron loss intensities and chemical structure of the molecule has not yet been examined in detail.

An observed (and calculated) differential cross section is an averaged quantity over the molecules randomly oriented with respect to the scattering electron. As a consequence, it is very difficult to recognize the effect of chemical structure.

The purpose of this project was to examine the preferential directions of the outgoing scattering electron for a selected fixed orientation of the molecule to find some general rules in the correlation of differential cross section (DCS) maps with the nature of excited mode or derivatives of multipoles.

Description of the work carried out during the visit

The idea was to plot three-dimensional diagrams resembling the electron density plots, but with the difference that instead of electron density the differential cross section for a selected vibrational mode is plotted. The wave vector of the incoming electron and the orientation of the molecule is fixed. We call these diagrams "spatial differential cross section (dcs) maps". In order to realize this aim following tasks were done:

1. Development a software for plotting the spatial dcs maps
2. Calculating and plotting spatial dcs maps in a systematic way:
 - a homonuclear diatomic (H₂),
 - a heteronuclear diatomic (HF),
 - a triatomic with dipole moment (H₂O).

The transition from the ground vibrational state, $v=0$, to the first excited state, $v=1$ was explored. Examined collision energy range was 1-30 eV.

For each molecule several maps were plotted for the \mathbf{k} vector of the incoming electron parallel and perpendicular to the dipole moment, and parallel or perpendicular to the molecular axes or bonds.

Theoretical model

In the DMR approach the body-frame DCS is directly obtained from inelastic transition matrix elements:

$$\frac{d\sigma}{d\Omega}(\vec{k}_{out} \leftarrow \vec{k}_{in}) = 16\pi^2 \left| \langle \vec{k}_{out} | \mathbf{T}_{10} | \vec{k}_{in} \rangle \right|^2$$

The two-channel DMR approach to DCS gives a set of integral equations:

$$\mathbf{T}_{10} = \mathbf{U}_{10} + \mathbf{U}_{10} \mathbf{G}_0 \mathbf{T}_{00} + \mathbf{U}_{11} \mathbf{G}_1 \mathbf{T}_{10}$$

In harmonic approximation the \mathbf{U}_{10} matrix is given as:

$$\mathbf{U}_{10} = \frac{1}{\sqrt{2}} \frac{\partial}{\partial q_k} \int e^{-ik_1 r} U e^{ik_2 r} d\mathbf{r}$$

where \mathbf{k}_2 is the incoming and \mathbf{k}_1 the outgoing vector

The main contribution to near-forward scattering comes from electrostatical interaction V_{stat} between electron and molecule.

Applying of the First Born approximation leads to the equation:

$$\mathbf{A}^B \equiv \mathbf{T}_{10}^B = \int e^{-ik_1 r} V_{stat} e^{ik_2 r} d\mathbf{r} = \frac{4\pi}{\mathbf{K}^2} \int e^{i\mathbf{K}r} \rho(\mathbf{r}) d\mathbf{r}$$

where \mathbf{A}^B is the scattering amplitude in the Born approximation and $\mathbf{K} = \mathbf{k}_2 - \mathbf{k}_1$ is the momentum

¹ R. Čurik, P. Čarsky, *J. Phys. B* **36**, (2003), 2165.

transfer.

Scattering amplitude is just a Fourier transform of the charge density divided by square of momentum transfer.

Using Taylor expansion for the exponential we obtain amplitude in terms of multipole contributions

$$A^B = \frac{4\pi}{K^2} \int \left[1 + i\mathbf{K}\mathbf{r} - \frac{1}{2}(\mathbf{K}\mathbf{r})^2 + \dots \right] \rho(\mathbf{r}) d\mathbf{r}$$

The first term represents integration over the total charge density and vanishes for a neutral molecule. The second term corresponds to the electron-permanent dipole interaction, and the third term to the quadrupole moment interaction.

Hence, the derivative of amplitude for the vibrationally inelastic transitions can be expressed as

$$\frac{\partial A^B}{\partial q_k} = \frac{4\pi}{K^2} \left[i\mathbf{K} \frac{\partial \mu}{\partial q_k} \mathbf{r} - \frac{1}{2} \mathbf{K}^T \frac{\partial \mathbf{M}}{\partial q_k} \mathbf{K} + \dots \right]$$

where μ is a dipole moment and M is the molecular second moment, closely related to quadrupole moment.

In near-forward scattering dipole term is high because of a small value of K in the denominator. Therefore the dipole term is a leading term in the near-forward direction and the scattering amplitude tends to its first Born approximation in this direction.

As can be seen, we also should expect near-forward scattering cross-section to be much higher for infra-red active modes because these exhibit nonzero derivative of the dipole moment.

Description of the main results obtained

H₂ molecule.

At small energy (2 eV) perpendicular collision vector results in DCS which is weakly directionally varied (DCS is nearly isotropic). Almost all directions of the scattering are of comparable probability, which is typical for s-wave scattering at low energies. Only the near-forward scattering is favoured to some extent.

For parallel incoming vector the axial symmetry is observed. The near-forward and near-backward directions are favoured. There is no scattering towards the 90 degree direction.

At higher energies and perpendicular collision vector the isotropy of the scattering disappears. The contour of the DCS becomes flat and narrow and arranged toward the forward direction. ***It is caused by the decreasing contribution of the perpendicular scattering.***

Perpendicular collision vector participates in scattering to 90 degrees in contrast to parallel collision vector which contributes only to near-forward and near backward scattering.

In the case of the parallel collision vector increase in energy leads to initial increasing and then decreasing of the forward scattering. For small energies the forward scattering is dominating, for higher energies the backward scattering dominates.

H₂ Conclusions:

The main contribution to DCS comes from the collision vector parallel to the H-H bond direction.

There is no such contribution to the scattering angle of 90 degree.

Dominance of backward scattering is observed as the collision energy is increased.

HF molecule.

DCS for very small angles is enormous compared with values for angles larger than 30 degree.

This is because of the fact that near-forward scattering is dominated by the derivative of the dipole potential.

At small energies for all orientations of the collision vector the contour of DCS tends to forward direction and follows the DCS for the first Born approximation potential. Only in the case of anti-parallel collision vector some backward scattering appears.

At higher energies the backward scattering appears also for the perpendicular collision vector. The scattering to 90 degree also appears for this vector.

At higher energy dipole contributions cease to be dominant and cross section reflects molecular structure to a large extent. Also backward scattering is largely increased.

This change is especially visible for parallel collision vector.

Near-forward scattering is favoured for all energies and for all directions of the collision vector. It results from the electron-dipole interaction. But the influence of this long-range potential decreases with the increasing energy of incoming electrons.

HF Conclusions:

In the case of a molecule with high dipole moment and an axial symmetry, and when the energy of collision electron is low, near-forward scattering can be replaced by the first Born potential scattering. The influence of long-range potential decreases with the increase of collision energy, as can be seen from FBA.

The main contribution to laboratory frame DCS comes from collision vectors parallel or anti-parallel to the dipole derivative vector or permanent dipole vector (both vectors indicate the same direction).

Dominance of backward scattering for the higher collision energies seems to indicate that energy transfer during the collision (e.g. vibrational excitation of molecules by the electron impact) is at these energies mainly driven by a short-range interaction which strongly affects large scattering angles.

H₂O molecule

Near-forward scattering is favored for all energies and for all directions of the collision vector for all vibrational modes of H₂O. This can be expected from the fact that all the vibrational modes of the water molecule are infra-red active and thus the dipole derivative for each mode is non-zero. The backward scattering increases with the increasing energy in contrast to the near-forward scattering.

Moving from linear molecule (when the derivative of the dipole moment, if any, and the molecular axis were the same) to polyatomic target allow us to realize that the property defining the shapes of DCS maps was not the derivative of the dipole but the symmetry axis. Presence of the non-zero derivative of the dipole moment just tells us there will be a peak for the small scattering angles.

Conclusions

It can be easily shown that for the considered molecular symmetries DCS maps must belong to the full symmetric irreducible representation of the molecular point group only for particular directions of the collision vector. For $D_{\infty h}$, $C_{\infty v}$ and C_{2v} symmetries these particular directions are parallel and anti-parallel to the molecular symmetry axis.

The shapes of the DCS maps lead to the following conclusions for an explanation of the mechanism of the energy transfer between colliding electrons and the vibrational motion of molecules. In a very rough approximation we can separate the colliding electrons into 2 groups.

1. The first group consists of electrons with a high impact parameter. These electrons interact weakly with the long-range part of the interaction, namely the derivative of the dipole moment with respect to the normal mode coordinate. They contribute to the peak of DCS in near forward direction. In case of IR inactive modes this process does not occur and the cross sections do not exhibit any peaks for the small scattering angles. Due to the weak nature of the interaction, this process is well described by the First Born Approximation. This mechanism is analogous to the one found in the vibrational IR spectroscopy.
2. Colliding electrons with the small impact parameter are described by a wave function with a nodal structure similar with the nodes of anti-bonding orbitals. The effect of the additional electron in such a continuum wave function is similar to the occupation of these anti-bonding orbitals. It leads to a weakening or strengthening of particular bonds which is reflected by

their elongation or shortening, respectively. Therefore the anti-bonding nodal structure of the continuum wave-function provides an effective method of the energy transfer into the vibrational motion of molecules.

The comparison of selected virtual orbitals and DCS maps for H_2 and H_2O molecules are presented in the figures 1-3.

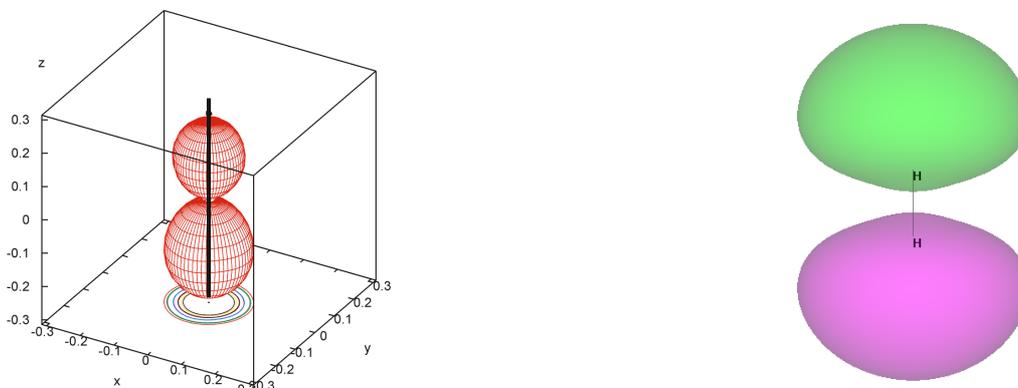


Fig 1. Left panel: DCS map for $e-H_2$ vibrational excitation. The collision vector is oriented along the z -axis and the energy is 10 eV. Right panel: anti-bonding orbital $1\sigma_u$ of H_2

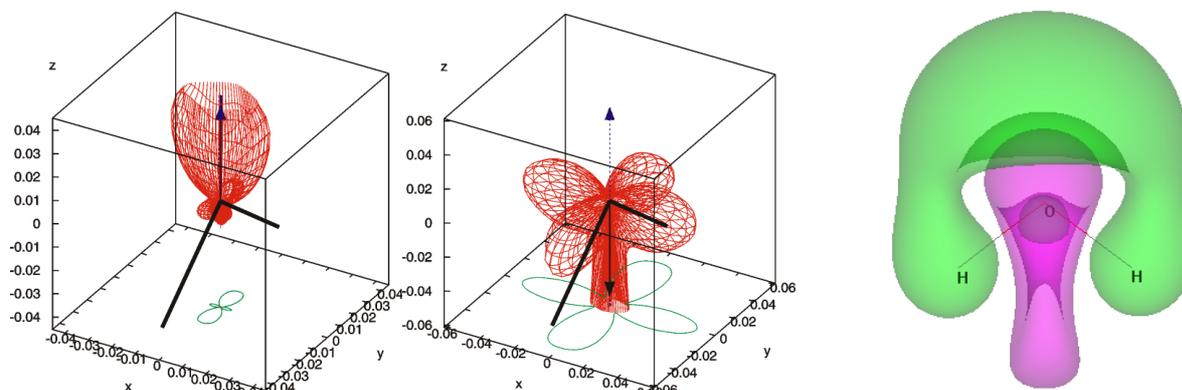


Fig 2. Left panel: DCS maps for $e-H_2O$ vibrational excitation (symm. stretch). The collision vector is oriented along the z -axis and the energy is 15 eV. Right panel: anti-bonding orbital A_1 of H_2O

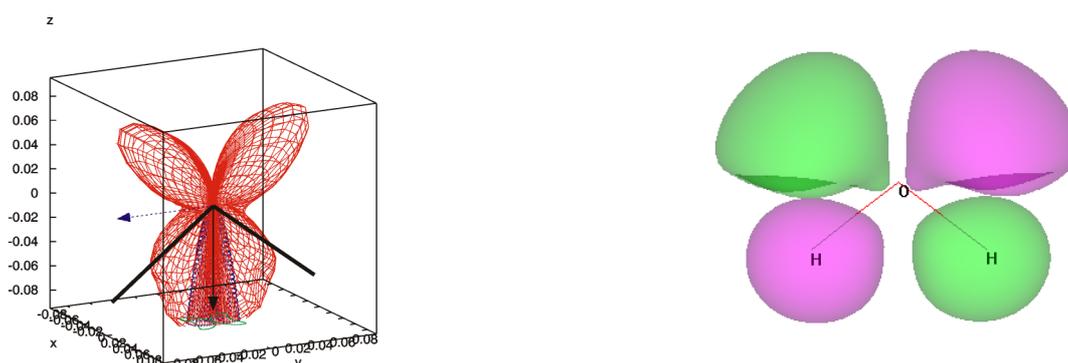


Fig 3. Left panel: DCS map for $e-H_2O$ vibrational excitation (asym. stretch). The collision vector is oriented along the z -axis and the energy is 15 eV. Right panel: anti-bonding orbital A_2 of H_2O

Projected publications/articles resulting or to result from the grant

The results presented in this report will be published in a joint paper with R. Čurík and P. Čarský From the host institution.