CALCULATIONS OF POLARIZABILITIES AND THEIR GRADIENTS FOR ELECTRON ENERGY-LOSS SPECTROSCOPY

Ivana PAIDAROVÁ[a1], Roman ČURÍK[a2,]* and Stephan P. A. SAUER[b]

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic; e-mail: [1] ivana.paidarova@jh-inst.cas.cz, [2] roman.curik@jh-inst.cas.cz

[b] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark; e-mail: sauer@kiku.dk

Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

We illustrate for a set of small hydrocarbons, CH_4, C_2H_4, C_3H_6 and C_3H_8, the important role of the electric dipole polarizability tensor and its geometric derivatives in theoretical models of electron energy-loss spectra (EELS). The coupled cluster linear response method together with Sadlej's polarized valence triple zeta basis set of atomic orbitals were used to calculate the polarizabilities and polarizability gradients. Incorporation of these *ab initio* data into the discrete momentum representation method (DMR) leads to perfect agreement between theory and collision experiments.

Keywords: Geometric derivatives of the electric dipole polarizability tensor; Coupled clusters linear response method; Electron energy-loss spectra; Discrete momentum representation method; DFT calculations; Hydrocarbons.

The discrete momentum representation (DMR) method[1,2] proved to be an efficient tool for theoretical studies of electron-molecule collisions namely at higher collision energies (above 10 eV). However at lower collision energies, where correlation forces play a dominant role, the DMR method predicted lower cross sections with resonance positions shifted to higher energies. The incorporation of a local correlation-polarization potential into the DMR method, recently suggested by Čuřík et al.[3], improved the performance of the method substantially and extended its applicability towards lower energies. For the construction of this correlation-polarization potential the authors proposed to use a short-range density functional theory (DFT) based correlation interaction that is smoothly connected to the

well-known asymptotic form defined by the molecular polarizability tensor. Furthermore, derivatives of the polarizability tensor with respect to the nuclear positions are required in order to build in the coupling between vibrational channels[2]. Polarizabilities as well as polarizability gradients can conveniently be obtained from various polarization propagator[4–6] or linear response function methods[7,8]. In this article we present for the series of small hydrocarbons, methane, ethene, cyclopropane and propane the necessary polarizability and polarizability gradient tensor components which were obtained from the coupled cluster singles and doubles linear response function[8] (CCSD-LR) using Sadlej's polarized valence triple zeta basis set (Sadlej-pVTZ)[9]. To our knowledge this is the first time that correlated values of the polarizability gradients with respect to nuclear cartesian coordinates are reported for these molecules. Furthermore we illustrate for methane and cyclopropane how crucial for good agreement with the EELS experiments it is to included the local correlation-polarization potential and thus the polarizability and its gradients in the DMR method.

METHODOLOGY

Calculation of Polarizability Gradient Tensor

Linear response methods at various levels of accuracy from self-consistent field (SCF) linear response theory[7,10] and time-dependent density functional theory (TD-DFT)[11] to the second order polarization propagator approximations, SOPPA [12–16] and SOPPA(CCSD)[15–17], multi-reference self-consistent-field linear response theory[7] and coupled cluster linear response theory[8,18] provide electromagnetic molecular properties that are able to meet continuously increasing experimental demands. Their application is only limited by the size of the molecular system and the available computer power. Correlated calculations of the electric dipole polarizability tensor are thus a common task for molecules in the ground electronic states, while calculations of polarizability gradients are found less frequently due to the computational cost. Polarizability gradients are otherwise required for the calculation of Raman intensities[19]. Normally they are obtained by numerical differentiation as e.g. implemented in the Dalton quantum chemistry program[20,21] at the SCF, MCSCF and DFT level, although at least one analytical implementation at the SCF level has been presented[22].

Recently, Vidal and Vazquez[23] have presented a very thorough study of the effects of all aspects of *ab initio* calculations of Raman intensities in small molecules such as the level of theory, basis set, step length in the

numerical differentiation and convergence thresholds. They concluded that calculations at the level of CCSD-LR are able to reproduce experimental values and that basis sets of polarized valence triple zeta quality like Dunning's aug-cc-pVTZ [24] are necessary. On the other hand, for calculations on larger molecules, such as the series of hydrocarbons treated here, they and other studies[15,25] suggest using Sadlej's polarized valence triple zeta basis sets[9] as best compromise between the computational demands and the accuracy of the results. We have therefore also employed Sadlej's basis set in the current work.

The gradients of the polarizability tensor components were evaluated numerically using a two-point formula, illustrated here for the *xx* component of polarizability tensor with respect to the *x* cartesian coordinate of nucleus A

$$\frac{\delta \alpha_{xx}}{\delta x_A} = \frac{\alpha_{xx}(R_{eq} + \Delta x_A) - \alpha_{xx}(R_{eq} - \Delta x_A)}{2\Delta x_A} \tag{1}$$

where R_{eq} denotes the equilibrium geometry. As displacement Δx_A we have chosen 0.0002 a.u. The numerical stability of this choice was tested for the CH_4 molecule by varying Δx_A from 0.0002 to 0.001 a.u. This value is in agreement with the findings of Rizzo and Pecul[26] and Vidal and Vazquez[23]. Before embarking on CCSD-LR calculations at all the distorted geometries, we have determined the minimal number of unique derivatives required by using the automated calculation at the SCF level implemented in the quantum chemistry program[20,21]. Due to the molecular symmetry, the number of necessary calculations is reduced by about 50% comparing with the complete set of displacements.

The bond distances for which the dipole polarizabilities and their derivatives have been evaluated slightly differ from the experimental equilibrium geometries. This small difference is necessary for consistency with the scattering model. The DMR scattering method treats the molecule at the SCF level and therefore we have employed equilibrium geometries (Table I) optimized with Sadlej's basis set at the SCF level.

Construction of DFT Hybrid Potential for EELS

The original DMR method[1,2] approximated the electron-molecule interaction with a static and exchange (SE) contributions. This can be compared with the SCF level of calculations in quantum chemistry. The lack of correlation interaction hindered its use for lower collision energies, i.e. energies com-

parable with the affinities of temporarily negative ions. Several electron-gas models for a potential that includes both correlation and polarization effects in electron-molecule scattering problems were proposed by Perdew and Zunger[27], O'Connell and Lane[39] and Padial and Norcross[28]. In contrast to most of the DFT potentials used in quantum chemistry these models do not contain exchange interaction and they are based on a hybridization of the local electron-gas theory for short distances and the asymptotic form of the polarization potential as

$$V_{cp} = \begin{cases} V_c, & r \le r_0 \\ V_p = -\dfrac{1}{2r^6} \displaystyle\sum_{i,j=1}^{3} \alpha_{ij} x_i x_j, & r > r_0 \end{cases} \tag{2}$$

TABLE I
Cartesian coordinates (in nm) optimized at the SCF level with Sadlej's polarized valence triple zeta basis set[a]

Molecule	Atom	x	y	z
CH_4	C	0.00000	0.00000	0.00000
	H1/H2	0.06269	±0.06269	0.06269
	H3/H4	–0.06269	±0.06269	∓0.06269
C_2H_4	C1/C2	±0.066108	0.000000	0.000000
	H1/H2	0.122875	±0.092569	0.000000
	H3/H4	–0.122875	∓0.092569	0.000000
C_3H_6	C1	0.000000	0.087688	0.000000
	C2/C3	±0.075940	–0.043844	0.000000
	H1/H2	0.000000	0.146299	±0.089873
	H3/H4	0.126698	–0.073149	±0.089873
	H5/H6	–0.126698	–0.073149	±0.089873
C_3H_8	C1	0.000000	0.000000	0.059036
	C2/C3	0.000000	±0.127959	–0.026248
	H1/H2	∓0.086955	0.000000	0.123936
	H3/H4	0.000000	±0.216687	0.036027
	H5/H6	±0.087638	0.132002	–0.090035
	H7/H7	∓0.087638	–0.132002	–0.090035

[a] The notation A/B together with the ± and ∓ signs implies that atom A has the cartesian coordinate with the upper sign, whereas atom B has the lower sign.

where r_0 is a matching radius where $V_c = V_p$ and α_{ij} is the static polarizability tenor of the molecule. In the above equation V_p is spherically symmetric in the case of the methane molecule. However, for less symmetric molecules the whole polarizability tensor α_{ij} has to be taken into account. The V_{cp} potential in Eq. (*2*) is energy independent and very simple to apply, it depends only on the molecular charge density and polarizabilities. For its short-range part V_c we followed the conclusions of Padial and Norcross[28] by choosing the form of Perdew and Zunger[27]

$$V_c(\mathbf{r}) = \begin{cases} 0.0311 \ln r_s - 0.0584 + 0.00133 r_s \ln r_s - 0.0084 r_s, & r_s < 1 \\ \dfrac{\gamma(1 + \frac{7}{6}\beta_1 \sqrt{r_s} + \frac{4}{3}\beta_2 r_s)}{(1 + \beta_1 \sqrt{r_s} + \beta_2 r_s)^2}, & r_s \geq 1 \end{cases} \tag{3}$$

where the constants are $\gamma = -0.1423$, $\beta_1 = 1.0529$, $\beta_2 = 0.3334$ and the radius of a unity charge r_s is a function of the bound-electron density $\rho(\mathbf{r})$

$$r_s = \left[\frac{3}{4\pi\rho(\mathbf{r})} \right]^{1/3}. \tag{4}$$

In order to calculate the vibrational coupling matrix elements (see ref.[2]) we also need to evaluate derivatives of V_{cp} with respect to nuclear coordinates. This leads to the necessity of knowing the derivatives of the dipole polarizabilities in Eq. (*2*) and through Eqs (*3*) and (*4*) also the derivatives of the electron density $\rho(\mathbf{r})$.

RESULTS AND DISCUSSION

Electric Dipole Polarizability and Polarizability Gradients

In Table II we show the components of the electric dipole polarizability tensors of methane, ethene, cyclopropane and propane calculated with the CCSD linear response function and Sadlej's polarized valence triple basis set at the reference geometry given in Table I. We can compare our CCSD-LR results with other recent correlated calculations for methane[15,29] and ethene[15,30–32]. Comparison with experimental or experiment based values[33,34], on the other hand, is not meaningful, because zero-point vibrational corrections are not included in our values.

TABLE II
Components of the electric dipole polarizability tensor (in a.u.) obtained at the CCSD-LR level with Sadlej's polarized valence triple zeta basis set

Molecule	α_{xx}	α_{yy}	α_{zz}
CH_4	16.41	16.41	16.41
C_2H_4	34.15	25.10	21.72
C_3H_6	37.81	37.81	32.84
C_3H_8	37.09	44.05	39.19

TABLE III
CH_4 derivatives (in a.u.) of the electric dipole polarizability tensor with respect to atomic cartesian coordinates, obtained at the CCSD-LR/Sadlej-pVTZ[a]

	α_{xx}	α_{xy}	α_{xz}	α_{yy}	α_{yz}	α_{zz}
$\frac{\partial}{\partial x_C}$	0.00	0.00	0.00	0.00	–5.15	0.00
$\frac{\partial}{\partial y_C}$	0.00	0.00	–5.15	0.00	0.00	0.00
$\frac{\partial}{\partial z_C}$	0.00	–5.15	0.00	0.00	0.00	0.00
$\frac{\partial}{\partial x_{H1/H2}}$	2.82	±1.33	±1.33	1.85	1.29	1.85
$\frac{\partial}{\partial y_{H1/H2}}$	±1.85	1.33	1.29	±2.82	±1.33	±1.85
$\frac{\partial}{\partial z_{H1/H2}}$	1.85	1.29	1.33	1.85	1.33	2.82
$\frac{\partial}{\partial x_{H3/H4}}$	–2.82	±1.33	∓1.33	–1.85	1.29	–1.85
$\frac{\partial}{\partial y_{H3/H4}}$	±1.85	–1.33	1.29	±2.82	∓1.33	±1.85
$\frac{\partial}{\partial z_{H3/H4}}$	∓1.85	1.29	–1.33	∓1.85	±1.33	∓2.82

[a] The notation $\frac{\partial}{\partial i_{A/B}}$ together with the ± and ∓ signs implies that the derivative with respect to the *i* coordinate of atom A has the upper sign, whereas the derivative with respect to atom B has the lower sign.

The agreement between our CCSD-LR value, 16.41 a.u., for the static polarizability of methane and the CCSD(T) value of 16.39 a.u., obtained by Maroulis[29] with a large non-standard basis set, is excellent. The same holds also for ethene, where our CCSD-LR values for the isotropic and anisotropic polarizability, 26.99 and 7.87 a.u., are in perfect agreement with the CC3/t-aug-cc-pVTZ values, 26.95 and 7.73 a.u., of Hald et al.[31] or the CCSD(T)/d-aug-cc-pCVTZ values, 26.98 and 7.75 a.u., of Raballand et al.[32].

We are not aware of any correlated calculations of the polarizability of cyclopropane or propane nor of any published values for the derivatives of the polarizability tensor with respect to cartesian nuclear coordinates. Tables III–VI report therefore, to our knowledge, for the first time correlated values of the components of the electric dipole polarizability gradients for all the four molecules included in our study. They were again obtained at the CCSD-LR/Sadlej-pVTZ level of theory.

Due to the lack of correlated literature values we have carried out a limited correlation study for the polarizability gradients ourselves. In the case of C_2H_4 we could afford to carry out finite field CCSD(T) calculations[35] but have observed only insignificant changes in the order of 1–2%. We con-

TABLE IV
C_2H_4 derivatives (in a.u.) of the electric dipole polarizability tensor with respect to atomic cartesian coordinates, obtained at the CCSD-LR/Sadlej-pVTZ level[a]

	α_{xx}	α_{xy}	α_{xz}	α_{yy}	α_{yz}	α_{zz}
$\frac{\partial}{\partial x_{C1/C2}}$	±5.73	0.00	±5.21	−2.23	0.00	±7.42
$\frac{\partial}{\partial y_{C1/C2}}$	0.00	∓4.01	0.00	0.00	0.00	0.00
$\frac{\partial}{\partial z_{C1/C2}}$	0.00	0.00	0.00	0.00	0.00	0.00
$\frac{\partial}{\partial x_{H1/H2}}$	4.03	±1.93	0.00	2.50	0.00	0.50
$\frac{\partial}{\partial y_{H1/H2}}$	±3.01	3.50	0.00	±5.24	0.00	±1.07
$\frac{\partial}{\partial z_{H1/H2}}$	0.00	0.00	−0.06	0.00	±0.48	0.00
$\frac{\partial}{\partial x_{H3/H4}}$	−4.03	∓1.93	0.00	−2.50	0.00	−0.50
$\frac{\partial}{\partial y_{H3/H4}}$	∓3.01	−3.50	0.00	∓5.24	0.00	∓1.07
$\frac{\partial}{\partial z_{H3/H4}}$	0.00	0.00	0.06	0.00	∓0.48	0.00

[a] See the footnote of Table III.

sider therefore the CCSD-LR values in Tables III–VI essentially to be converged with respect to electron correlation.

In order to provide accurate polarizability gradients also for larger molecules, we have to consider other methods than CCSD-LR which becomes too demanding with increasing molecule size. A less demanding alternative could be the SOPPA(CCSD) method[17], which has been shown to give frequency dependent polarizabilities and van der Waals coefficients in close agreement with CCSD-LR [15–17,36] as well as NMR spin-spin coupling con-

TABLE V
C_3H_6 derivatives (in a.u.) of the electric dipole polarizability tensor with respect to atomic cartesian coordinates, obtained at the CCSD-LR/Sadlej-pVTZ level[a]

	α_{xx}	α_{xy}	α_{xz}	α_{yy}	α_{yz}	α_{zz}
$\frac{\partial}{\partial x_{C1}}$	0.00	5.00	0.00	0.00	0.00	0.00
$\frac{\partial}{\partial y_{C1}}$	3.27	0.00	0.00	4.81	0.00	−2.42
$\frac{\partial}{\partial z_{C1}}$	0.00	0.00	0.00	0.00	−4.36	0.00
$\frac{\partial}{\partial x_{C2/C3}}$	±6.01	0.68	0.00	±0.98	0.00	∓2.09
$\frac{\partial}{\partial y_{C2/C3}}$	1.57	±2.52	0.00	−5.60	0.00	1.21
$\frac{\partial}{\partial z_{C2/C3}}$	0.00	0.00	∓3.78	0.00	2.18	0.00
$\frac{\partial}{\partial x_{H1/H2}}$	0.00	−0.02	±0.38	0.00	0.00	0.00
$\frac{\partial}{\partial y_{H1/H2}}$	0.32	0.00	0.00	4.54	±2.15	2.50
$\frac{\partial}{\partial z_{H1/H2}}$	±1.17	0.00	0.00	±3.74	3.46	±4.49
$\frac{\partial}{\partial x_{H3/H4}}$	3.01	−1.59	±1.71	1.20	∓0.77	2.16
$\frac{\partial}{\partial y_{H3/H4}}$	−1.76	0.91	∓0.77	−0.67	±0.82	−1.25
$\frac{\partial}{\partial z_{H3/H4}}$	±3.01	∓1.12	3.00	±1.81	−1.73	±4.49
$\frac{\partial}{\partial x_{H5/H6}}$	−3.01	−1.59	±1.71	−1.20	±0.77	−2.16
$\frac{\partial}{\partial y_{H5/H6}}$	−1.76	−0.91	±0.77	−0.67	±0.82	−1.25
$\frac{\partial}{\partial z_{H5/H6}}$	±3.01	±1.12	−3.00	±1.81	−1.73	±4.49

[a] See the footnote of Table III.

C_3H_8 derivatives (in a.u.) of the electric dipole polarizability tensor with respect to atomic cartesian coordinates, obtained at the CCSD-LR/Sadlej-pVTZ level[a]

	α_{xx}	α_{xy}	α_{xz}	α_{yy}	α_{yz}	α_{zz}
$\dfrac{\partial}{\partial x_{C1}}$	0.00	0.00	–6.44	0.00	0.00	0.00
$\dfrac{\partial}{\partial y_{C1}}$	0.00	0.00	0.00	0.00	4.42	0.00
$\dfrac{\partial}{\partial z_{C1}}$	–5.15	0.00	0.00	5.12	0.00	–3.02
$\dfrac{\partial}{\partial x_{C2/C3}}$	0.00	∓0.97	5.41	0.00	0.00	0.00
$\dfrac{\partial}{\partial y_{C2/C3}}$	∓0.38	0.00	0.00	∓1.11	–4.62	∓0.46
$\dfrac{\partial}{\partial z_{C2/C3}}$	5.02	0.00	0.00	–5.82	∓1.17	1.54
$\dfrac{\partial}{\partial x_{H1/H2}}$	∓4.62	0.00	3.46	∓1.71	0.00	∓3.29
$\dfrac{\partial}{\partial y_{H1/H2}}$	0.00	∓0.89	0.00	0.00	0.21	0.00
$\dfrac{\partial}{\partial z_{H1/H2}}$	2.63	0.00	∓2.32	0.42	0.00	4.20
$\dfrac{\partial}{\partial x_{H3/H4}}$	0.00	±1.19	–0.04	0.00	0.00	0.00
$\dfrac{\partial}{\partial y_{H3/H4}}$	±1.21	0.00	0.00	±7.64	2.56	±2.04
$\dfrac{\partial}{\partial z_{H3/H4}}$	0.38	0.00	0.00	4.20	±2.10	2.21
$\dfrac{\partial}{\partial x_{H5/H6}}$	±4.67	1.04	–2.81	±1.91	∓0.69	±2.66
$\dfrac{\partial}{\partial y_{H5/H6}}$	0.30	±0.84	∓0.10	0.53	–0.18	0.08
$\dfrac{\partial}{\partial z_{H5/H6}}$	–2.73	∓0.45	±1.95	–0.68	0.86	–3.22
$\dfrac{\partial}{\partial x_{H7/H8}}$	∓4.67	–1.04	–2.81	∓1.91	∓0.69	∓2.66
$\dfrac{\partial}{\partial y_{H7/H8}}$	–0.30	∓0.84	∓0.10	–0.53	–0.18	–0.08
$\dfrac{\partial}{\partial z_{H7/H8}}$	–2.73	∓0.45	∓1.95	–0.68	–0.86	–3.22

[a] See the footnote of Table III.

TABLE VII
C_3H_8 derivatives (in a.u.) of the electric dipole polarizability tensor with respect to atomic cartesian coordinates, obtained at the SOPPA(CCSD)/Sadlej-pVTZ level[a]

	α_{xx}	α_{xy}	α_{xz}	α_{yy}	α_{yz}	α_{zz}
$\frac{\partial}{\partial x_{C1}}$	0.00	0.00	−6.48	0.00	0.00	0.00
$\frac{\partial}{\partial y_{C1}}$	0.00	0.00	0.00	0.00	4.55	0.00
$\frac{\partial}{\partial z_{C1}}$	−5.14	0.00	0.00	5.26	0.00	−2.97
$\frac{\partial}{\partial x_{C2/C3}}$	0.00	∓0.99	5.43	0.00	0.00	0.00
$\frac{\partial}{\partial y_{C2/C3}}$	∓0.36	0.00	0.00	∓1.01	−4.70	∓0.40
$\frac{\partial}{\partial z_{C2/C3}}$	5.01	0.00	0.00	−5.94	∓1.15	1.51
$\frac{\partial}{\partial x_{H1/H2}}$	∓4.56	0.00	3.45	∓1.68	0.00	∓3.29
$\frac{\partial}{\partial y_{H1/H2}}$	0.00	∓0.84	0.00	0.00	0.18	0.00
$\frac{\partial}{\partial z_{H1/H2}}$	2.60	0.00	∓2.30	0.41	0.00	4.12
$\frac{\partial}{\partial x_{H3/H4}}$	0.00	±1.15	−0.06	0.00	0.00	0.00
$\frac{\partial}{\partial y_{H3/H4}}$	±1.17	0.00	0.00	±7.57	2.54	±2.01
$\frac{\partial}{\partial z_{H3/H4}}$	0.37	0.00	0.00	4.24	±2.08	2.21
$\frac{\partial}{\partial x_{H5/H6}}$	±4.60	1.05	−2.79	±1.88	∓0.71	±2.65
$\frac{\partial}{\partial y_{H5/H6}}$	0.29	±0.80	∓0.09	0.50	−0.15	0.06
$\frac{\partial}{\partial z_{H5/H6}}$	−2.71	∓0.46	±1.93	−0.67	0.85	−3.15
$\frac{\partial}{\partial x_{H7/H8}}$	∓4.60	−1.05	−2.79	∓1.88	∓0.71	∓2.65
$\frac{\partial}{\partial y_{H7/H8}}$	−0.29	∓0.80	∓0.09	−0.50	−0.15	−0.06
$\frac{\partial}{\partial z_{H7/H8}}$	−2.71	∓0.46	∓1.93	−0.67	−0.85	−3.15

[a] See the footnote of Table III.

stants in excellent agreement with experiment[37]. In particular isotope effects as well as temperature shifts in the NMR spin-spin coupling constants, which both depend on the coupling constant gradients, could be reproduced with SOPPA(CCSD)[38].

In Table VII we present therefore polarizability gradients for propane obtained at the SOPPA(CCSD)/Sadlej-pVTZ level. Comparison with the CCSD-LR results in Table VI shows very good agreement between both approaches. The maximum deviation is 0.14 a.u. or 2.7%, while the mean and mean absolute devations are only –0.01 and 0.03 a.u., respectively. Although these are only results for one molecule, one can expect a similar good performance for other larger hydrocarbons, which makes SOPPA(CCSD) also for this property, i.e. the polarizability gradients, an interesting alternative to CCSD-LR, because it has a better relation between accuracy and computational effort.

Spectra and Impact of the DFT Hybrid Potential

Figure 1 shows the calculated electron energy-loss spectra (EELS) for the methane molecule obtained by two approaches. The broken curve shows the results when correlation-polarization forces were omitted, while the full curve represents the calculated spectra with the hybrid form of correlation as summarized in Eqs (2) and (3). The left panel displays data for a collision energy E_c = 5 eV and the right panel is for E_c = 20 eV. The spectra clearly show two distinct bands. The deformation band around the energy loss of 180 meV made of the ν_2 and ν_4 modes and the stretch band around 360 meV formed by the ν_1 and ν_3 modes. Our calculated spectra were obtained as follows: the calculated cross-sections, which would predict spectra with zero width, were spread with an energy width determined from the elastic peak (the peak with the zero energy loss) of the measured spectra. We used a normalized Lorentzian shape to mimic the experimental data.

It can be noticed that for the higher collision energies the effect of the correlation interaction is very weak as the bound molecular orbitals have a shorter time to respond to the presence of the external field brought by the scattering electron. However, in the case of E_c = 5 eV the impact of correlation-polarization forces is dramatically visible. It is clear that proper incorporation of such forces becomes essential for describing electron-molecule dynamics at lower energies.

Figure 2 summarizes the EELS for the cyclopropane molecule. Again the comparison between the uncorrelated and correlated results is given for a
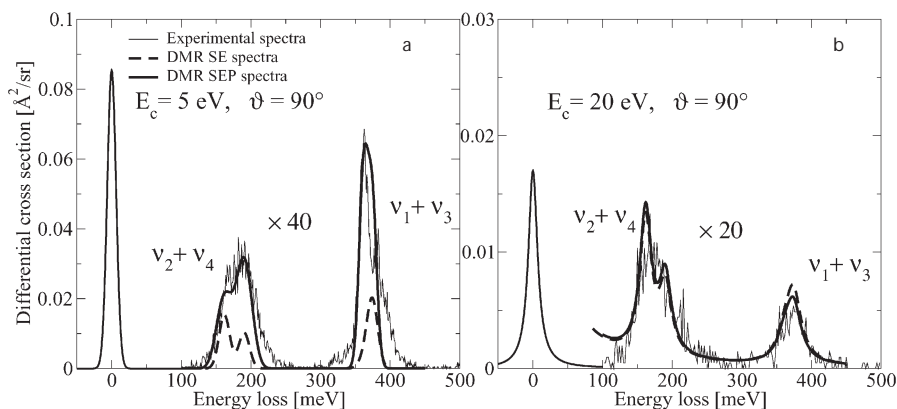
FIG. 1

Computed and measured electron energy-loss spectra of methane for a scattering angle $\vartheta = 90°$. Collision energy $E_c = 5$ eV (a) and $E_c = 10$ eV (b). The broken curve represents calculated results in absence of the correlation-polarization forces while the full curve displays spectra with the present model for the correlation-polarization interaction. Experimental data were measured by Allan[3] (2008)
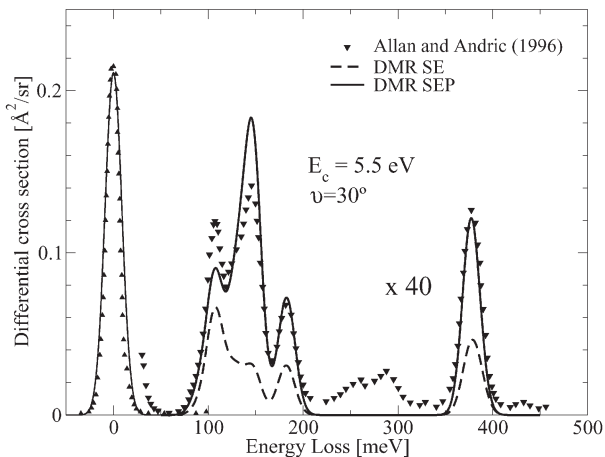

FIG. 2

Computed and measured electron energy-loss spectra of cyclopropane for a scattering angle $\vartheta = 30°$. Collision energy $E_c = 5.5$ eV. Calculated results in absence of the correlation-polarization forces (– – –), spectra with the present model for the correlation-polarization interaction (——). Experimental data were taken from Allan and Andric[40] (1996)

low collision energy of E_c = 5.5 eV. In this case the vibrational structure is richer with two major bands. The lower band (100–200 meV) is formed by the C–C vibrations and the C–H deformation modes. The upper band (around 370 meV) consists of C–H stretch modes. The weak band filling the space between these two major bands is attributed to the overtones of the lower band and therefore it is absent in the DMR calculations as DMR neglects the overtones completely. Also for the cyclopropane molecule we notice again the dramatic effects of the correlation-polarization energy on the calculated spectra.

CONCLUSIONS

In the first step we have employed the CCSD linear response method in combination with Sadlej's polarized valence triple zeta basis set in calculations of the electric dipole polarizability and its gradient for four small hydrocarbons. The reported CCSD-LR polarizability gradients of methane, ethene, cyclopropane and propane are to our knowledge the first correlated values report in the literature for this property. For the static polarizability of methane and ethene we find very good agreement with previous coupled cluster results including triples corrections. For propane we have also investigated the performance of the SOPPA(CCSD) method in the calculation of the polarizability gradients and found very good agreement with the computationally much more demanding CCSD-LR results. This makes SOPPA(CCSD) an interesting alternative for the calculation of polarizability gradients for large organic molecules.

In the second step we have used the calculated polarizability tensor, together with its gradient, to construct the long-range part of the correlation-polarization interaction used in the DMR method. That allowed us to perform theoretical modeling of the low-energy EEL spectra for the methane and cyclopropane molecules. We have found the correlation-polarization energy to be essential for a proper description of the electron-molecule dynamics at collision energies around 5 eV. The agreement of our calculated EELS with the available experimental data is very good. The DMR calculations for the other two studied molecules are under development and the results will be published elsewhere.

REFERENCES

1. Polášek M., Juřek M., Ingr M., Čársky P., Horáček J.: *Phys. Rev. A* **2000**, *61*, 032701.
2. Čurík R., Čársky P.: *J. Phys. B: At. Mol. Opt. Phys.* **2003**, *36*, 2165.
3. Čurík R., Čársky P., Allan M.: *J. Phys. B: At. Mol. Opt. Phys.* **2008**, *41*, 115203.
4. a) Linderberg J., Öhrn Y.: *Propagators in Quantum Chemistry*. Academic Press, London 1973; b) Oddershede J.: *Adv. Quantum Chem.* **1978**, *2*, 275; c) Jørgensen P., Simons J.: *Second Quantization-Based Methods in Quantum Chemistry*. Academic Press, New York 1981; d) Oddershede J. in: *Methods in Computational Molecular Physics* (G. H. F. Diercksen and S. Wilson, Eds), pp. 249–271. D. Reidel Publ. Co, Dordrecht 1983; e) Oddershede J.: *Adv. Chem. Phys.* **1987**, *69*, 201; f) Oddershede J. in: *Methods in Computational Molecular Physics* (S. Wilson and G. H. F. Diercksen, Eds), pp. 303–324. Plenum Press, New York 1992.
5. Oddershede J., Jørgensen P., Yeager D. L.: *Comput. Phys. Rep.* **1984**, *2*, 33.
6. Sauer S. P. A., Packer M. J. in: *Computational Molecular Spectroscopy* (P. R. Bunker and P. Jensen, Eds), Chap. 7, pp. 221–252. John Wiley and Sons, London 2000.
7. Olsen J., Jørgensen P.: *J. Chem. Phys.* **1985**, *82*, 3235.
8. a) Koch H., Jørgensen P.: *J. Chem. Phys.* **1990**, *93*, 3333; b) Christiansen O., Jørgensen P., Hättig C.: *Int. J. Quantum Chem.* **1998**, *68*, 1.
9. Sadlej A. J.: *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995.
10. a) Peng H. W.: *Proc. R. Soc. London, Ser. A.* **1941**, *178*, 499; b) Langhoff P. W., Epstein S. T., Karplus M.: *Rev. Mod. Phys.* **1972**, *44*, 602; c) McLachlan A. D., Ball M. A.: *Rev. Mod. Phys.* **1964**, *36*, 844; d) Rowe D. J.: *Rev. Mod. Phys.* **1968**, *40*, 153.
11. Casida M. E. in: *Recent Development and Applications of Modern Density Functional Theory* (M. J. Seminario, Ed.), p. 391. Elsevier, Amsterdam 1996.
12. Nielsen E. S., Jørgensen P., Oddershede J.: *J. Chem. Phys.* **1980**, *73*, 6238.
13. a) Packer M. J., Dalskov E. K., Enevoldsen T., Jensen H. J. Aa., Oddershede J.: *J. Chem. Phys.* **1996**, *105*, 5886; b) Bak K. L., Koch H., Oddershede J., Christiansen O., Sauer S. P. A.: *J. Chem. Phys.* **2000**, *112*, 4173; c) Nielsen C. B., Sauer S. P. A., Mikkelsen K. V.: *J. Chem. Phys.* **2003**, *119*, 3849; d) Olsen J., Jørgensen P., Helgaker T., Oddershede J.: *J. Phys. Chem. A* **2005**, *109*, 11618.
14. a) Sauer S. P. A., Diercksen G. H. F., Oddershede J.: *Int. J. Quantum Chem.* **1991**, *39*, 667; b) Parkinson W. A., Sauer S. P. A., Oddershede J., Bishop D. M.: *J. Chem. Phys.* **1993**, *98*, 487; c) Sauer S. P. A., Oddershede J.: *Int. J. Quantum Chem.* **1994**, *50*, 317; d) Packer M. J., Sauer S. P. A., Oddershede J.: *J. Chem. Phys.* **1994**, *100*, 8969; e) Packer M. J., Dalskov E. K., Sauer S. P. A., Oddershede J.: *Theor. Chim. Acta* **1994**, *89*, 323.
15. Dalskov E. K., Sauer S. P. A.: *J. Phys. Chem. A* **1998**, *102*, 5269.
16. a) Sauer S. P. A., Oddershede J.: *Int. J. Quantum Chem.* **1994**, *50*, 317; b) Paidarová I., Sauer S. P. A.: *Adv. Quantum Chem.* **2005**, *48*, 185; c) Sauer S. P. A., Paidarová I.: *Comp. Lett.* **2007**, *3*, 399; d) Paidarová I., Sauer S. P. A.: *Collect. Czech. Chem. Commun.* **2008**, *73*, 1415.
17. Sauer S. P. A.: *J. Phys. B: At. Mol. Opt. Phys.* **1997**, *30*, 3773.
18. a) Monkhorst H. J.: *Int. J. Quantum Chem. Symp.* **1977**, *11*, 421; b) Mukherjee D., Mukherjee P. K.: *Chem. Phys.* **1979**, *39*, 325; c) Ghosh S., Mukherjee D., Bhattacharyya S. N.: *Chem. Phys. Lett.* **1982**, *72*, 161; d) Dalgaard E., Monkhorst H. J.: *Phys. Rev. A* **1983**, *28*, 1217; e) Aiga F., Sasagane K., Itho R.: *Int. J. Quantum Chem.* **1994**, *51*, 87;

f) Kobayashi R., Koch H., Jørgensen P.: *Chem. Phys. Lett.* **1994**, *219*, 30; g) Datta B., Sen P., Mukherjee D.: *J. Phys. Chem.* **1995**, *99*, 6441.

19. a) Svendsen E. N., Tanega J.: *J. Raman. Spectrosc.* **1978**, *7*, 268; b) Svendsen E. N., Oddershede J.: *J. Chem. Phys.* **1979**, *71*, 3000; c) Gough K. M., Murphy W. F., Stroyer-Hansen T., Svendsen E. N.: *J. Chem. Phys.* **1987**, *87*, 341; d) Gough K. M.: *J. Chem. Phys.* **1989**, *91*, 2424; e) Gough K. M., Dwyer J. R.: *J. Phys. Chem. A* **1998**, *102*, 2723; f) Gough K. M., Dwyer J. R., Dawes R.: *Can. J. Chem.* **2000**, *78*, 1035; g) Neugebauer J., Reiher M., Hess B. A.: *J. Chem. Phys.* **2002**, *117*, 8623; h) Quinet Q., Champagne B., Kirtman B.: *Int. J. Quantum Chem.* **2002**, *89*, 341; i) Smirnov K. S., Bougeard D.: *J. Raman. Spectrosc.* **2006**, *37*, 100.

20. Angeli C., Bak K. L., Bakken V., Christiansen O., Cimiraglia R., Coriani S., Dahle P., Dalskov E., Enevoldsen T., Fernandez B., Hättig C., Hald K., Heiberg H., Helgaker T., Hettema H., Jensen H. J. Aa., Jonsson D., Jørgensen P., Kirpekar S., Klopper W., Kobayashi R., Koch H., Ligabue A., Lutnas O. B., Mikkelsen K. V., Norman P., Olsen J., Packer M. J., Pedersen T. B., Rinkevicius Z., Rudberg E., Ruden T. A., Ruud K., Salek P., Sanchez de Merás A., Saue T., Sauer S. P. A., Schimmelpfennig B., Sylvester-Hvid K. O., Tayler P. R., Vahtras O., Wilson D. J., Agren H.: *Dalton, A Molecular Electronic Structure Program*, Release 2.0. http://www.kjemi.uio.no/software/dalton/dalton.html, 2005.

21. Helgaker T., Ruud K., Bak K. L., Jørgensen P., Olsen J.: *Faraday Discuss.* **1994**, *99*, 165.

22. a) Quinet Q., Champagne B.: *J. Chem. Phys.* **2001**, *115*, 6293; b) Quinet Q., Champagne B., Kirtman B.: *J. Comput. Chem.* **2001**, *22*, 1920.

23. a) Vidal L. N., Vazquez P. A. M.: *Quim. Nova* **2003**, *26*, 507; b) Vidal L. N., Vazquez P. A. M.: *Int. J. Quantum Chem.* **2005**, *103*, 632.

24. a) Dunning T. H., Jr.: *J. Chem. Phys.* **1989**, *90*, 1007; b) Kendall R. A., Dunning T. H., Harrison R. J.: *J. Chem. Phys.* **1992**, *96*, 6796; c) Woon D. E., Dunning T. H., Jr.: *J. Chem. Phys.* **1993**, *98*, 1358; d) Woon D. E., Dunning T. H., Jr.: *J. Chem. Phys.* **1994**, *100*, 2975; e) Woon D. E., Dunning T. H., Jr.: *J. Chem. Phys.* **1995**, *103*, 4572; f) Wilson A. K., Woon D. E., Peterson K. A., Dunning T. H., Jr.: *J. Chem. Phys.* **1999**, *110*, 7667.

25. a) Halls M. D., Schlegel H. B.: *J. Chem. Phys.* **1999**, *111*, 8819; b) van Caillie C., Amos R. D.: *Phys. Chem. Chem. Phys.* **2000**, *2*, 2123.

26. a) Pecul M., Rizzo A.: *J. Chem. Phys.* **2002**, *116*, 1259; b) Pecul M., Coriani S.: *Chem. Phys. Lett.* **2002**, *355*, 327.

27. Perdew J. P., Zunger A.: *Phys. Rev. B* **1981**, *23*, 5048.

28. Padial N. T., Norcross D. W.: *Phys. Rev. A* **1984**, *29*, 1742.

29. Maroulis G.: *Chem. Phys. Lett.* **1994**, *226*, 420.

30. Maroulis G.: *J. Chem. Phys.* **1992**, *97*, 4188.

31. Hald K., Pawlowski F., Jørgensen P., Hättig C.: *J. Chem. Phys.* **2003**, *118*, 1292.

32. Raballand W., Rotger M., Boudon V., Loëte M., Breidung J., Thiel W.: *J. Mol. Struct.* **2006**, *780–781*, 79.

33. Thomas G. F., Meath W. J.: *Mol. Phys.* **1977**, *34*, 113.

34. Jhanwar B. L., Meath W. J., MacDonald J. C. F.: *Can. J. Chem.* **1983**, *61*, 1027.

35. Maroulis G.: *J. Mol. Struct. (THEOCHEM)* **2003**, *633*, 177.

36. Sánchez M., Ferraro M. B., Alkorta I., Elguero J., Sauer S. P. A.: *J. Chem. Phys.* **2008**, *128*, 64318.

37. a) Enevoldsen T., Oddershede J., Sauer S. P. A.: *Theor. Chem. Acc.* **1998**, *100*, 275; b) Kirpekar S., Sauer S. P. A.: *Theor. Chem. Acc.* **1999**, *103*, 146; c) Sauer S. P. A., Raynes W. T.: *J. Chem. Phys.* **2000**, *113*, 3121; d) Grayson M., Sauer S. P. A.: *Mol. Phys.* **2000**, *98*,

1981; e) Provasi P. F., Aucar G. A., Sauer S. P. A.: *J. Chem. Phys.* **2001**, *115*, 1324; f) Krivdin L. B., Sauer S. P. A., Peralta J. E., Contreras R. H.: *Magn. Reson. Chem.* **2002**, *40*, 187; g) Barone V., Provasi P. F., Peralta J. E., Snyder J. P., Sauer S. P. A., Contreras R. H.: *J. Phys. Chem. A* **2003**, *107*, 4748; h) Sauer S. P. A., Krivdin L. B.: *Magn. Reson. Chem.* **2004**, *42*, 671; i) Provasi P. F., Sauer S. P. A.: *J. Chem. Theory Comput.* **2006**, *2*, 1019.

38. a) Wigglesworth R. D., Raynes W. T., Sauer S. P. A., Oddershede J.: *Mol. Phys.* **1997**, *92*, 77; b) Wigglesworth R. D., Raynes W. T., Sauer S. P. A., Oddershede J.: *Mol. Phys.* **1998**, *94*, 851; c) Sauer S. P. A., Møller C. K., Koch H., Paidarová I., Špirko V.: *Chem. Phys.* **1998**, *238*, 385; d) Wigglesworth R. D., Raynes W. T., Kirpekar S., Oddershede J., Sauer S. P. A.: *J. Chem. Phys.* **2000**, *112*, 736; e) Wigglesworth R. D., Raynes W. T., Kirpekar S., Oddershede J., Sauer S. P. A.: *J. Chem. Phys.* **2000**, *112*, 3735; f) Sauer S. P. A., Raynes W. T., Nicholls R. A.: *J. Chem. Phys.* **2001**, *115*, 5994.

39. O'Connell J., Lane N. F.: *Phys. Rev. A* **1983**, *27*, 1893.

40. Allan M., Andric L.: *J. Chem. Phys.* **1996**, *105* 3559.