

Nuclear dynamics in resonant inelastic X-ray scattering and X-ray absorption of methanol

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We report on a combined **theoretical and experimental** study of core-excitation spectra of gas and liquid phase methanol as obtained with use of X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS). The electronic transitions are studied with complementary computational methods including strict and extended second-order algebraic diagrammatic construction (ADC(2) and ADC(2)-x), restricted active space second-order perturbation theory (RASPT2), and time-dependent density functional theory (TDDFT) – providing a complete assignment of the near oxygen *K*-edge XAS. We show that multimode nuclear dynamics is of crucial importance for explaining the available experimental XAS and RIXS spectra. The multimode nuclear motion was considered in a recently developed *mixed representation* where dissociative states and highly excited vibrational modes are accurately treated with a time-dependent wave packet technique while the remaining active vibrational modes are described using Franck–Condon amplitudes. Particular attention is paid to the polarization dependence of RIXS and the effects of the isotope substitution on the RIXS profile in the case of dissociative core-excited states. Our approach predicts the splitting of the $2a''$ RIXS peak to be due to an interplay between molecular and pseudo-atomic features arising in the course of transitions between dissociative core- and valence-excited states. The dynamical nature of the splitting of the $2a''$ peak in RIXS of liquid methanol near pre-edge core excitation is shown. The theoretical results are in good agreement with **our liquid phase measurements and gas phase experimental data available from literature**.

I. INTRODUCTION

Soft X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) are powerful techniques in studies of the molecular electron structure as it provides insights into the local properties in the vicinity of preselected core-excited atoms in polyatomic systems. Two forms of RIXS are recognized as the final state is either (i) a valence-excited electronic state or (ii) a vibrationally excited state of the electronic ground state in which case the scattering process is also referred to as resonant quasi-elastic X-ray scattering. In particular the latter form of RIXS can deliver detailed information about the nuclear dynamics and interatomic potentials

because of the lack of inhomogeneous broadening. Extended regions of the ground state potential can be probed, since the nuclear wave packet can move far away from the equilibrium in the intermediate state as will be amply demonstrated in the present work. In a combination of XAS and RIXS, we study the electronic and vibrational structures of methanol in the gas phase. Methanol, CH_3OH , is an important compound used in several practical applications such as *e.g.* renewable fuels and hydrogen storage mediums. In addition, CH_3OH is of principal interest because, in its liquid form, it is a system that like water^{1–3} is dominated by hydrogen-bond interactions^{4–7} – although it is noted that the replacement of a hydrogen by a methyl group in going from water to methanol gives rise to an amphiphilic character of the latter as well as different solvent properties.

The properties of liquid methanol has been thoroughly explored using many different experimental techniques including neutron diffraction⁸, X-ray diffraction^{4,8,9}, X-ray emission

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spectroscopy (XES)¹⁰, XAS¹¹, and RIXS¹². In our study, we focus on **theory of methanol** in the gas phase and on providing an accurate assignment of the associated XAS and RIXS spectra at the oxygen *K*-edge, **available from literature**^{13–15}. Our study is motivated by the lack of a comprehensive theoretical study of the X-ray spectra of this system and will serve as an important stepping stone to understand the corresponding spectra in the liquid phase **obtained in the present work**. The O 1s X-ray absorption spectra of gas phase methanol were investigated by different groups^{13–15}. Usually the assignment of the O 1s pre-edge XAS spectrum is made by means of calculations based on semi-empirical methods^{13–15}, but an exception is found in Ref.¹¹ where the transition-potential density functional theory (TP-DFT) approach was adopted. However, the TP-DFT is not truly a method based on first-principles as, most notably, the charge of the core hole in the creation of the transition potential functions in practice is a spectral tuning parameter and, furthermore, a detailed spectral assignment is absent in this article. Therefore, the first aim of our study is to shed light on the electronic core-excited states which form the pre-edge XAS of gas phase methanol using high-level *ab initio* quantum chemical calculations^{16–19}. Another shortcoming of most previous studies is the neglect of nuclear quantum dynamics, although it was demonstrated through the RIXS measurements in gas phase methanol¹⁵ and in the liquid phase¹² that there is a strong sensitivity of the high-energy RIXS peak to isotopic substitution. This observation makes it timely to investigate the role of nuclear dynamics in both XAS and RIXS spectra of this important system. The developed theoretical approach used in our simulations of nuclear dynamics in methanol is similar to the one used in our earlier studies of the RIXS spectrum of water^{20–23} with the key difference being the treatment of a larger number of normal modes.

The paper is organized as follows. In Sec. II, we outline the multimode theory of XAS and RIXS, using a so-called mixed representation. The computational methods are described in Sec. III. In Sec. IV A, we present the results of calculations of the XAS spectrum. We start the study of RIXS, in Sec. IV B, by considering the quasi-elastic channel. In the subsequent section, Sec. IV C, we present the results of simulations of RIXS for different final and core-excited states taking into account only the electronic degrees of freedom. Finally, in Sec. IV B 4, we discuss the pseudo-atomic band and the role of isotopic substitution on RIXS profile. Our findings are summarized in Sec. V.

II. THEORY AND METHODOLOGY

A. Time-dependent picture

We study the RIXS process starting from the multimode vibrational state of the ground state, characterized by the vector of vibrational quantum numbers $\mathbf{v}_0 = (v_0^{(0)}, v_0^{(1)}, v_0^{(2)}, \dots)$, and ending up in the multimode vibrational state $\mathbf{v}_f = (v_f^{(0)}, v_f^{(1)}, v_f^{(2)}, \dots)$ of the final electronic state. We adopt the

time-dependent representation for the XAS $\sigma(\omega)$ and RIXS $\sigma(\omega', \omega)$ cross-sections^{21,24,25}

$$\begin{aligned}\sigma_{\text{abs}}(\omega) &= \text{Re} \sum_c \langle \mathbf{v}_0 | \tilde{\Psi}(0) \rangle, \\ \sigma(\omega', \omega) &= \frac{1}{\pi} \text{Re} \int_0^\infty e^{i(\omega - \omega' - \omega_{f0} + \varepsilon_{v_0} + i\Gamma_f)t} \sigma(t) dt, \\ \sigma(t) &= \langle \Psi(0) | \Psi(t) \rangle, \\ |\Psi(0)\rangle &= i \sum_{v_c} \frac{D_{fc} |v_c\rangle \langle v_c | D_{c0} |v_0\rangle}{\omega - \omega_{c0} + \varepsilon_{v_0} - \varepsilon_{v_c} + i\Gamma} \\ &= D_{fc} \int_0^\infty e^{i(\omega - \omega_{c0} + \varepsilon_{v_0} + i\Gamma)t} |\psi_c(t)\rangle dt,\end{aligned}\tag{1}$$

where the wave packet $\tilde{\Psi}(0)$ is given by the same equation as $\Psi(0)$ except that both $D_{fc} = (\mathbf{e}' \cdot \mathbf{d}_{fc})$ and $D_{c0} = (\mathbf{e} \cdot \mathbf{d}_{c0})$ should be replaced by \mathbf{d}_{c0} . The RIXS process with the scattering amplitude $F_{v_f} = -i \langle v_f | \Psi(0) \rangle$ is affected by nuclear dynamics in the core-excited state and in the final (ground) state as represented in the nuclear wave packets

$$|\psi_c(t)\rangle = e^{-ih_c t} D_{c0} |v_0\rangle, \quad |\Psi(t)\rangle = e^{-ih_f t} |\Psi(0)\rangle.\tag{2}$$

Here (ω, \mathbf{e}) and (ω', \mathbf{e}') are the frequencies and polarization vectors of incoming and scattered photons, respectively, ω_{ij} is the spacing between minima of the potential energy surfaces of the electronic states i and j , with $i, j = 0, c, f$ denote the ground 0, core-excited c and final f electronic states, respectively; Γ and Γ_f are the lifetime broadenings of the core-excited and final states, respectively. **Note that throughout the text Γ refers to the half-width at half-maximum value.** The transition amplitudes $D_{fc} = (\mathbf{e}' \cdot \mathbf{d}_{fc})$ and $D_{c0} = (\mathbf{e} \cdot \mathbf{d}_{c0})$ depend on the scalar product of polarization vectors and corresponding dipole moments of electronic transitions. In the simulations, we employ the Born–Oppenheimer (BO) approximation, assuming a small influence of coupling between dynamics in different excited states.

B. Mixed representation and the mD+nD model

It is quite common in electronically excited states, that some degrees of freedom are dissociative or they are excited above the dissociation limit. They require special treatment due to the continuity of the vibrational spectrum^{20,21,23}. The best numerical method for continuum states is the time-dependent wave packet technique^{24,25}. Since degrees of freedom which have bound potentials can be treated more efficiently in frequency domain, we will use a mixed representation for the cross section. The m modes will be described using the time-dependent wave packet technique while the remaining n modes are treated using the stationary method of Franck–Condon (FC) amplitudes. Let us write the total nuclear hamiltonian as a sum of two independent terms

$$h_i = h_i^{(m)} + h_i^{(n)}, \quad i = 0, c, f,\tag{3}$$

neglecting the coupling between the selected subspaces of vibrational modes. We will look for the solution of the Schrödinger equation with the Hamiltonian h_i in the mixed (time-energy) representation as the product of wave packet $\psi_i^{(m)}(t)$ and eigenfunction $|v_i\rangle = |v_i^{(1)}, v_i^{(2)}, \dots, v_i^{(n)}\rangle$

$$\begin{aligned} & |\psi_i^{(m)}(t)\rangle |v_i\rangle, \\ & i \frac{\partial}{\partial t} |\psi_i^{(m)}\rangle = h_i^{(m)} |\psi_i^{(m)}\rangle, \\ & h_i^{(n)} |v_i\rangle = \varepsilon_{v_i} |v_i\rangle. \end{aligned} \quad (4)$$

The m degrees of freedom are described in the time domain, while the stationary Schrödinger equation is used for the rest of the n modes $|v_i\rangle$. Consequently, the initial vibrational state in general eq.(2) should be replaced as follows

$$|v_0\rangle \rightarrow |\mu_0\rangle |v_0\rangle, \quad \varepsilon_{v_0} \rightarrow \varepsilon_{\mu_0} + \varepsilon_{v_0}. \quad (5)$$

Here $(|\mu_0\rangle, \varepsilon_{\mu_0})$ and $(|v_0\rangle, \varepsilon_{v_0})$ are the eigenfunctions and eigenvalues of the ground state hamiltonians $h_0^{(m)}$ and $h_0^{(n)}$, respectively. Using a condition of completeness, $1 = \sum |v_c\rangle \langle v_c|$, and $\exp(-ih_it) = \exp(-ih_i^{(n)}t) \exp(-ih_i^{(m)}t)$, one can get the following expression for the wave packet (2)

$$\begin{aligned} |\psi_c(t)\rangle &= e^{-ih_c^{(n)}t} |v_0\rangle e^{-ih_c^{(m)}t} D_{c0} |\mu_0\rangle \\ &= \sum_{v_c} e^{-i\varepsilon_{v_c}t} |v_c\rangle \langle v_c | v_0 \rangle |\psi_c^{(m)}(t)\rangle, \\ |\psi_c^{(m)}(t)\rangle &= e^{-ih_c^{(m)}t} D_{c0} |\mu_0\rangle. \end{aligned} \quad (6)$$

Now we are at liberty to rewrite the expression for the wave packet $|\Psi(0)\rangle$ (1)

$$\begin{aligned} |\Psi(0)\rangle &= \sum_{v_c} |v_c\rangle \langle v_c | v_0 \rangle |\Psi_{v_c}(0)\rangle, \\ |\Psi_{v_c}(0)\rangle &= D_{fc} \int_0^\infty e^{i(\omega - \omega_{c0} + \varepsilon_{v_0} + \varepsilon_{\mu_0} - \varepsilon_{v_c} + i\Gamma)t} |\psi_c^{(m)}(t)\rangle dt \end{aligned} \quad (7)$$

and for the wave packet $|\Psi(t)\rangle$ (2)

$$\begin{aligned} |\Psi(t)\rangle &= e^{-ih_f^{(n)}t} e^{-ih_f^{(m)}t} \sum_{v_c} |v_c\rangle \langle v_c | v_0 \rangle |\Psi_{v_c}(0)\rangle \\ &= \sum_{v_f} \sum_{v_c} e^{-i\varepsilon_{v_f}t} |v_f\rangle \langle v_f | v_c \rangle \langle v_c | v_0 \rangle |\Psi_{v_c}(t)\rangle, \\ \Psi_{v_c}(t) &= e^{-ih_f^{(m)}t} \Psi_{v_c}(0). \end{aligned} \quad (8)$$

Here we used the expression in eq. (7) for $|\Psi(0)\rangle$ and the condition of the completeness $1 = \sum |v_f\rangle \langle v_f|$. Using the orthonormality of the vibrational states $\langle v_f | v_f' \rangle = \delta_{v_f, v_f'}$ and the insertion of eqs. (7) and (8) into eq. (1), one can compute the autocorrelation function $\sigma(t)$ (1). This allows us to formulate the employed expression for the RIXS cross section in

the mixed (mD+nD) representation

$$\begin{aligned} \sigma_{\text{abs}}(\omega) &= \text{Re} \sum_{v_c} |\langle v_0 | v_c \rangle|^2 \langle \mu_0 | \tilde{\Psi}_{v_c}(0) \rangle, \\ \sigma(\omega', \omega) &= \frac{1}{\pi} \text{Re} \sum_{v_f v_c' v_c} \langle v_0 | v_c' \rangle \langle v_c' | v_f \rangle \langle v_f | v_c \rangle \langle v_c | v_0 \rangle \\ &\quad \times \int_0^\infty e^{i(\omega - \omega' - \omega_{f0} - \varepsilon_{v_f} + \varepsilon_{v_0} + \varepsilon_{\mu_0} + i\Gamma_f)t} \sigma_{v_c' v_c}(t) dt, \\ \sigma_{v_c' v_c}(t) &= \langle \Psi_{v_c'}(0) | \Psi_{v_c}(t) \rangle, \end{aligned} \quad (9)$$

where $\tilde{\Psi}_{v_c}(0)$ is defined similarly as $\tilde{\Psi}(0)$ (see eq.(1)).

C. Polarization dependence

In the current study, we will ignore the change of the transition dipole moment during the course of nuclear motion and we use the equilibrium values for \mathbf{d}_{c0} and \mathbf{d}_{fc} . Since we explore the XAS and RIXS spectra of gas phase methanol, the cross-sections should be averaged over isotropic molecular orientations using equations^{25,26} $\langle \mathbf{e} \cdot \mathbf{d}_{c0} \rangle^2 = d_{c0}^2/3$ and

$$\begin{aligned} & \overline{(\mathbf{e} \cdot \mathbf{d}_{c0})(\mathbf{e} \cdot \mathbf{d}_{c0})(\mathbf{e}' \cdot \mathbf{d}_{fc})(\mathbf{e}' \cdot \mathbf{d}_{fc})} \\ &= \frac{d_{c0}^2 d_{fc}^2}{30} [3 + \cos^2 \chi + (1 - 3 \cos^2 \chi)(\hat{\mathbf{d}}_{fc} \cdot \hat{\mathbf{d}}_{c0})^2], \end{aligned} \quad (10)$$

where $\chi = \angle(\mathbf{e}, \mathbf{k}')$ is the angle between polarization vector of incoming photon and momentum of outgoing one, $\hat{\mathbf{d}} = \mathbf{d}/d$ is the unit vector along \mathbf{d} . To illustrate the role of polarization, let us consider core-excitation to a state of A' symmetry, with the transition dipole moment $\mathbf{d}_{\mathcal{A}'}$, and de-excitation to final states of A' or A'' symmetry, with decay transition dipole moments $\mathbf{d}_{A'}$ and $\mathbf{d}_{A''}$, respectively. Taking into account that the transition dipole moments to the states of A' and A'' symmetry are orthogonal, $(\mathbf{d}_{\mathcal{A}'} \cdot \mathbf{d}_{A''}) = 0$, we get

$$\begin{aligned} \sigma_{\mathcal{A}' A''} &\propto d_{\mathcal{A}'}^2 d_{A''}^2 (3 + \cos^2 \chi), \\ \sigma_{\mathcal{A}' A'} &\propto d_{\mathcal{A}'}^2 d_{A'}^2 [3 + \cos^2 \chi + (1 - 3 \cos^2 \chi)(\hat{\mathbf{d}}_{\mathcal{A}'} \cdot \hat{\mathbf{d}}_{A'})^2]. \end{aligned} \quad (11)$$

Bear in mind that the transition dipole moments $\mathbf{d}_{\mathcal{A}'}$ and $\mathbf{d}_{A'}$ are not necessary parallel to each other, in spite that both lie in the molecular plane.

D. Electronic structure theory calculations

The ground-state electronic configuration of methanol is $(1a')^2, (2a')^2, (3a')^2, (4a')^2, (1a'')^2, (5a')^2, (6a')^2, (7a')^2, (2a'')^2$, where the $1a'$ -orbital is the atomic oxygen $1s$ -orbital. To shed light on the electronic structure of the methanol molecule in the ground state and the O $1s$ core-excited states, it is useful to consider the natural orbitals. Fig. 1 shows the occupied natural orbitals which we obtained from the restricted active space self-consistent field (RASSCF)²⁷ calculation (see Sec. III) of the ground state. The unoccupied natural orbitals $\phi_i = 8a', 9a', 3a'', 10a', 11a'$, and $12a'$ are obtained from separate calculations for each core-excited state

$|\Phi_i\rangle = |1a'^{-1}\phi_i\rangle$, where $1s_O = 1a'$. In spite of the fact that we use multi-configurational approaches, we adopt, for brevity, a one-electron $|1a'^{-1}\phi_i\rangle$ notation for the total wavefunction. Thereby, we specify the largest contribution in the multi-electron wave function $|\Phi_i\rangle$, where the occupation number of the natural orbital ϕ_i exceeds 90%. Hence, we assign the singlet core-excited states according to the orbital which is unoccupied in the ground state and receives the core-electron in the course of photoabsorption. We use the capital letters for multi-electron states to distinguish them from one-electron orbitals in lowercase letters

$$\begin{aligned} |8\mathcal{A}'\rangle &= |1a'^{-1}8a'^1\rangle, & |9\mathcal{A}'\rangle &= |1a'^{-1}9a'^1\rangle, \\ |3\mathcal{A}''\rangle &= |1a'^{-1}3a''^1\rangle, \dots \end{aligned} \quad (12)$$

The same notation for the multi-electron states is used in the single-reference propagator-based calculations of the excited states but the excitation vectors (the eigenvectors of the respective secular equation) refer in these cases to canonical Hartree–Fock or Kohn–Sham orbitals.

Underlying the simulations of nuclear dynamics as described above, we performed limited scans of the potential energy surfaces of the electronic ground state and the low-lying oxygen core-excited states. Prior to addressing the excited states, we determined the global minimum of the electronic ground state and found the associated normal mode coordinates along which we explored the potentials of the collection of electronic states involved in the XAS and RIXS processes. The DFT method is widely employed to determine ground state molecular structures and vibrational frequencies of polyatomic systems with reliable agreement to the experiment and we adhere to this choice (see Sec. III for details). For instance, the vibrational frequencies of methanol as here obtained with the B3LYP hybrid functional^{28,29} display an agreement with the experiment results reported in Ref.³⁰ that exceeds what is found at the complete active space second order perturbation theory (CASPT2) framework^{16,17}, see Table I. Relying on the results of the normal mode analysis, we constructed the 1D potential energy curves (PECs) along the corresponding normal modes obtained with the DFT method, as described in Sec. III. The subsequent simulations of the XAS and RIXS spectra were performed in the framework of the (1D+3D)-model neglecting mode couplings, as described in further detail in Sec. IV A 2.

In particular for unbound core-excited states, the time-dependent wave packet approach will probe the PECs far away from the equilibrium and we therefore use the multi-reference RAS model for their construction with active spaces adequate to correctly treat the dissociation limit. The core-excited states are all constructed with a common set of orbitals by means of the technique of state-averaging and these states are thus internally orthogonal, but they are nonorthogonal to and interacting with the ground state. This aspect is an artifact of the approach that in principle makes a calculation of transition properties gauge-origin dependent but which in practice is of minor concern for core-excited states and also handled with the RAS-state interaction (RASSI) approach^{31,32}. The main advantage with a separate-state (averaged or not) optimization of core-excited states is the very efficient treatment

of the electronic relaxation.

In a propagator or response theory approach, the core-excited states are only indirectly referenced by the solving of secular equations in the frequency-domain and after introducing the core-valence separation (CVS) approximation^{33,34}. With this approach, all states are noninteracting and the calculation of transition properties is gauge-origin independent as long as an appropriate truncation of multipole moment expansions is made^{35–38}. An appropriate treatment of electronic relaxation in the core-excited state requires the inclusion of double-electron excitation operators and we have for that reason adopted the second-order ADC polarization propagator method, which has been shown to provide an excellent description of core-excitation processes¹⁸ in the Franck–Condon region. For reference, we will also provide conventional CVS-based time-dependent DFT (TDDFT) calculations of the XAS spectrum of methanol. Standard Kohn–Sham TDDFT is, however, based on a reference state parameterization restricted to single-excitations and it can therefore not lead to a proper description of relaxation effects. Nevertheless, it is known that CVS-TDDFT calculations of core-electron absorption and emission spectra show a good agreement with experiment once the large self-interaction error inflicted spectral shifts are accounted for¹⁹.

As an alternative to adopting the CVS approximation, it has been shown possible to address X-ray spectroscopies by means of the complex polarization propagator (CPP) approach^{39–42}, which has recently been combined with ADC⁴³. By introducing relaxation mechanisms and finite lifetimes of excited states, the CPP approach defines complex response functions in the frequency domain with real and imaginary parts that are related by Kramers–Kronig relations³⁹. A frequency region embedded in the spectrum, such as the oxygen *K*-edge region in the present work, can be addressed without any approximations made in the construction of the propagator (such as for example the CVS approximation), and this has in turn enabled the derivation and implementation of the *full* electronic polarization propagator for inelastic scattering such as RIXS⁴⁴. We will apply this CPP/ADC method to study the RIXS of methanol and we note that in regions where the intermediate core-excited states are close in energy, our approach will be particularly advantageous as it encompasses the complete channel interaction between all intermediate states^{25,26}.

III. COMPUTATIONAL DETAILS

The geometry optimization and Hessian calculation were performed in C_s symmetry on the level of DFT/B3LYP^{28,29} functional and aug-cc-pVTZ basis set⁴⁵ in the Gaussian09 software⁴⁶, from which the vibrational frequencies (see Table I) and Wilson coordinate displacements of the normal modes were derived. For comparison, we also determined the equilibrium geometry and normal modes in the CASPT2 framework^{16,17} with ANO-RCC-VTZP⁴⁷ basis set (see Table I) using the MOLCAS program (version 8.2)⁴⁸ without imposing symmetry and with 12 electrons in an active space of 12 orbitals. For the calculation of core- and valence-

excited states and correspondent transition dipoles moments we used three different methods (RASPT2, CPP-ADC(2), and TDDFT), which are described in details below.

The computation of ground and core-excited states were performed with the RASSCF method⁴⁹ followed by RASPT2⁵⁰. These calculations were scalar relativistic, as implemented the MOLCAS code (version 8.2)⁴⁸ using the Douglas-Kroll-Hess formulation^{51,52} and the ANO-RCC-VTZP⁴⁷ basis set. The transition dipole moments between the studied electronic states were calculated within the RASSI approach^{31,32}. The core-excitation energies and transition dipole moments presented as RASPT2 in Tab. II were computed at the equilibrium geometry, using an extended Rydberg basis set (8s8p6d) and the C_1 symmetry. Proper treatment of the transition dipole moments is ensured by using the “highly-excited-state” (HEXS) approach⁵³ within the RASSCF method. The three orbitals having atomic orbital characters $C1s$ ($2a'$), combinations of $O2s+C2s$ ($3a'$) and $O2s-C2s$ ($4a'$) were kept inactive. The $O1s$ ($1a'$) orbital was frozen and placed in a separate part of the active space where its occupancy could be controlled to two for the ground and valence-excited states and to one for core-excited states. The full active space consisted of 11 orbitals; Namely, the $O1s$ orbital, four of the occupied orbitals having valence character: $1a''$, $5a'$, $6a'$, $7a'$, $2a''$; and the six lowest unoccupied orbitals: $8a'$, $9a'$, $3a''$, $10a'$, $11a'$ and $12a'$. The ground state was obtained by a state-specific calculation while a state-averaging over 7 roots was employed for the core-excited states.

Calculations of core-excitation energies and ground-to-core-excited state transition moments were also performed at the CVS-ADC(2)-x/d-aug-cc-pVTZ level of theory. In addition complex dipole polarizabilities and RIXS scattering amplitudes were computed at the CPP-ADC(2) approach and the aug-cc-pVTZ basis set. All ADC calculations were performed using a developers version of Q-Chem 5.0⁵⁴.

The PECs of ground and core-excited states were computed along the distortion vectors of 11 normal modes. Because the torsion mode ν_{12} (Table I) has too low frequency (0.036 eV) to be resolved in a RIXS experiment, this mode was excluded from our calculations. The PECs scans were performed with state specific RASPT2 calculations of the ground state (A' symmetry) and the lowest valence excited state of A'' symmetry (to enable studies of electronically inelastic RIXS processes) as described above, but with a smaller diffuse Rydberg basis (4s4p2d). For the core-excited states PECs, we performed a state-averaging over four electronic states for A' symmetry and over two states for A'' symmetry. To increase the computational efficiency while computing the PECs, we constrained the symmetry whenever possible. Hence, for the vibrational modes of A' symmetry, we used the C_s point group, whereas for the A'' symmetry the C_1 constrain was considered. One should mention that the use or not of symmetry constrains did not significantly affect the energies of the valence- and core-excited states in our simulations.

The TDDFT calculations were performed with the NWChem program⁵⁵ using the restricted energy window (REW) approach, which in essence is the same as the CVS approximation. The range-separated CAMB3LYP functional⁵⁶

was used with the parameterization proposed in Ref.⁴⁰ for core-excitations and in conjunction with Dunning’s aug-cc-pVTZ basis set⁴⁵.

Based on the core-transitions calculated with above methods, the XAS and RIXS cross-sections (eq. (9)) were calculated with use of a modified version of the *eSPec* program²³. The numerical solution of the equations presented in Sec. II B was carried out as described in ref.²³. The main reason for why the proposed scheme is more numerically efficient than carrying out a full $m+n$ -dimensional wave packet propagation is related to the intermediate wave packet calculation. Within the discrete variable representation, the number of integrals required to solve eq. (7) is equal to the total number of points in the grid $N^{(n+m)}$, N being the number of grid points along each dimension. Instead, we only need to solve $k \times N^n$ integrals, where k is the total number of intermediate states included in the m -dimensional Franck-Condon partition. Furthermore, we employ the fast Fourier transform (FFT) to solve eq. (7). Thus, by taking advantage of the shift theorem, the solution of the integral is reduced to performing N^n FFT evaluations and computing the required 1D Franck-Condon amplitudes.

IV. RESULTS AND DISCUSSION

A. X-ray absorption

Although the XAS spectrum is formed by electron-vibrational transitions, it is instructive to start by presenting the pure electronic core-excitations, which determine the skeleton of the total XAS profile.

1. Electronic contributions to XAS

The XAS was computed using three different quantum chemical tools (RASPT2, ADC(2)-x, TDDFT) described in Sec. III. The results of calculations of oscillatory strengths f and transition energies are collected in Table II. The corresponding XAS cross-sections (Fig. 2), computed with $\Gamma = 0.08$ eV and neglecting nuclear motion, display rather strong sensitivity of the XAS profile to the theoretical method. The oscillatory strength f is derived from the different quantum chemical approximations, but we plot the XAS cross sections using the following equation (in SI units) for the cross section at resonance⁵⁷

$$\sigma(\omega_{\text{res}}) = f \frac{e^2}{2m_e c \epsilon_0 \Gamma}. \quad (13)$$

We will see below that the theory (Fig. 2) can not properly reproduce the experiment without taking into account nuclear degrees of freedom. Due to this we postpone the comparison of the RASPT2, ADC(2)-x and TDDFT methods with experiment until Sec. IV A 2.

2. Role of nuclear motion in XAS

The methanol molecule has 12 vibrational modes, which are presented in Table I. The mode assignment and experimental frequencies are taken from ref.³⁰. To understand the influence of nuclear motion on the XAS, we start with determination of which normal modes are active. This is done by comparing the PECs of the core-excited states with the ground state PEC; in each state computed along the normal coordinate Q of 11 modes using the RASPT2 method (see Sec. III). Let us remind that the torsion mode ν_{12} is excluded in our simulations because of its too low frequency to influence the spectra. The PECs of the ground and core-excited states of the five active vibrational modes are collected in Fig. 3.

The selected modes are: ν_1 (OH-stretching) which is dissociative in the $8A'$ core-excited state, ν_8 (CO-stretching) which is pseudo-dissociative in the $8A'$ and $9A'$ core-excited states, and ν_7 , ν_6 , ν_5 (CH_3 -rock, OH-bending, and CH_3 s-deformation, respectively) each of which have a shift of the minimum upon core-excitation. The remaining vibrational modes are not active because the PECs of core excited states are very similar to the PECs of the ground state (see Appendix A and Fig. 15). Furthermore, only a sub-set of four modes (out of the five modes in Fig. 3) are active for each individual core-excited state

$$\begin{aligned}
 8A' &: 1D(\nu_1) + 3D(\nu_8, \nu_5, \nu_6) \\
 9A' &: 1D(\nu_8) + 3D(\nu_7, \nu_5, \nu_6) \\
 3A'' &: 1D(\nu_8) + 3D(\nu_7, \nu_5, \nu_6) \\
 10A' &: 1D(\nu_8) + 3D(\nu_7, \nu_5, \nu_6) \\
 11A' &: 1D(\nu_7) + 3D(\nu_8, \nu_5, \nu_6) \\
 12A' &: 1D(\nu_7) + 3D(\nu_8, \nu_5, \nu_6).
 \end{aligned} \tag{14}$$

Here we order the vibrational modes according to the $1D+3D$ model outlined in Sec. II B as a general $mD+nD$ representation. Hence, for each core-excitation, the mixed representation treats one mode in time domain and three modes in frequency domain. This subselection shown in eq. (14) was performed as follows. Mode ν_1 was included only for the $8A'$ state, since the PECs are not shifted with respect to the GS for the remaining states (Fig. 3). Mode ν_7 was excluded only for the $8A'$ state, based on the same shift criterion. To ensure the accuracy of this selection we carried out 1D calculations of XAS and RIXS for each mode.

The XAS cross section, in which nuclear dynamics is taken into account, is computed in the framework of the $1D+3D$ model using eq.(9) and $\Gamma = 0.08$ eV as the lifetime broadening of the O1s core-hole. Here and below we neglect the dependence of the transition dipole moment on nuclear coordinates, taking \mathbf{d}_{c0} as calculated at the equilibrium geometry. Results of the simulation are depicted in Fig. 4.

Comparison of the computed XAS profiles without (Fig. 2) and with nuclear dynamics (Fig. 4) shows the importance of nuclear motion for an accurate description of the XAS. This is because the PECs are different for distinct core-excited states. To demonstrate clearly the effect of nuclear degrees of freedom on the XAS profile we present an additional spectrum, in which the same transition dipole moment was deliberately

used for all core-excited states (see Fig. 4). The main effect is seen already in the strong broadening and intensity reduction of the first ($8A'$) XAS peak. The reason for this is that PEC of ν_1 mode becomes repulsive under core-excitation, similar to gas phase and liquid water^{2,3}, where the molecule dissociates into a Hydrogen atom and a core-excited methoxy radical CH_3O^* . We see that the agreement with experiment¹⁴ improves for all theoretical methods when the nuclear motion is taken into account. One should notice that the ADC(2)-x and RASPT2 methods give better agreement with the experiment¹⁴ both from the point of view of intensity distribution as well as the peak positions (Fig. 4). Let us note that here we compare the transition dipole moments and core-excitation energies from different methods, whereas the PEC shapes are taken from the RASPT2 calculations in all cases, as described in Sec. III.

B. Quasi-elastic resonant X-ray scattering: Nuclear dynamics

In this Section, we consider the RIXS which ends up in the electronic ground state and focus on two lowest core excited states $8A'$ (Fig. 5) and $9A'$ (Fig. 6). As one can see from the PECs (Fig. 3), the methanol dissociates along the OH bond in the first core-excited state, $8A'$, while all modes have bound PECs for the second core-excited state, $9A'$. This is the main reason for such strong difference in the vibrational progression of $8A'$ and $9A'$ RIXS channels. The RIXS spectra are simulated in the framework of the $1D+3D$ model as it was outlined in Sec. II B, just as the XAS spectra presented above. Again, we use the BO approximation and assume that the vibrational modes are uncoupled. We employed the same active vibrational modes as selected for the simulation of XAS (eq. (14)) because only the ground and core-excited states participate in the quasi-elastic RIXS process.

1. The RIXS via the dissociative $8A'$ core-excited state

When the photon energy is tuned in resonance with the $8A'$ state, the methanol molecule dissociates along the OH bond (Fig. 3). The small mass of hydrogen means that the nuclear wave packet can move far away from equilibrium along the OH bond during the core-hole life-time in the dissociative PEC of the $8A'$ state. This results in population of high ν_1 vibrational levels upon decay to the ground state and explains the origin of the extensive progression in RIXS for the OH stretching mode (Fig. 5). This progression forms the so-called molecular band^{24,25} with its maximum at $\omega - \omega' = 0$. The other vibrational modes remain bound under core-excitation and hence their vibrational progressions are much shorter. Therefore the role of the remaining vibrational modes is only "to dress" the OH skeleton in overtones, as seen in the lower panel of Fig. 5. We characterize the vibrational resonances in RIXS by $n = (\nu_1, \nu_8, \nu_6, \nu_5)$ composed of the active modes in this channel (see eq. (14)).

Due to ultra-fast dissociation along the OH bond, with kinetic energy release of about 3 eV, the nuclear wave packet

has time to reach the region of dissociation during the lifetime of the core-excited state. **The decay transition in the fragment of dissociation, the core-excited methoxy radical (CH_3O^*), results in the appearance of a peak at $\omega - \omega' \approx 8$ eV, which we named as atomic-like peak, following the well-established terminology used for ultra-fast dissociation in diatomic molecules^{24,25,58}. It is worth mentioning that the atomic-like peak has the same energy as so-called pseudo-atomic peak, which in contrast is formed near the equilibrium. We will discuss the atomic-like and pseudo-atomic peaks in detail in the Sec. IV B 4. Note that the width of the atomic-like peak is significantly larger than the natural broadening $\Gamma = 0.08$ eV (Fig. 5). The reason for this is the vibrational structure of the methoxy radical.**

2. Control of the nuclear dynamics via the variable scattering duration

As it is well known, the RIXS profile is very sensitive to the scattering duration^{25,59}

$$\tau = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}} \quad (15)$$

which is controlled by detuning from the top of the XAS resonance $\Omega = \omega - \omega_{\text{top}}$. To make the picture complete it is instructive to explore the Ω dependence of the RIXS spectra around the $8A'$ absorption resonance, as shown in Fig. 7.

One can see, as we tune below the top of absorption, that the atomic-like peak gradually vanishes (Fig. 7). The intensity of this peak drops down sufficiently already at $\Omega = -0.5$ eV and it disappears completely already at $\Omega = -0.75$ eV. Simultaneously to the quenching of the atomic-like peak, one can see the shortening of the vibrational progression with increase of $|\Omega|$. Both these observations are due to the shortening of the scattering duration, so that the wave packet propagates only a short distance away from the equilibrium. Finally, the whole RIXS profile collapses to the Rayleigh line^{60,61} at $\Omega < -1.5$ eV.

Another effect related to energy detuning is the purification of the RIXS spectra when $|\Omega|$ increases. As observed from Fig. 7, the intensity of the overtones related to the soft modes (Fig. 5) decreases faster than high frequency OH stretching mode⁶². Already at $\Omega = -0.75$ eV one can barely see overtones and only the main ν_1 vibrational progression remains. This is because the other modes has no time to perform a oscillation when the period is longer than the scattering duration

$$\tau < T_{\text{vib}} = \frac{2\pi}{\omega_{\text{vib}}}. \quad (16)$$

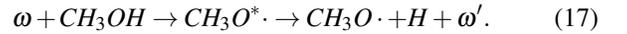
3. The RIXS via the bound $9A'$ core-excited state

Let us turn our attention to the RIXS through the second core-excited state $9A'$ shown in Fig. 6. Here we assigned vibrational resonances of ground state by $n = (\nu_8, \nu_7, \nu_6, \nu_5)$ according to eq. (14). Contrary to RIXS through $8A'$ (Fig. 5) the

OH stretching mode is not active in this channel. Therefore we see a significant shortening of the vibrational progression which is confined in the region $0 \leq \omega - \omega' \lesssim 1$ eV. This is because the core-excited wave packet does not propagate far from the equilibrium due to the bound nature of the PECs. The core-excited dynamics at $9A'$ state is mostly affected by the ν_8 and ν_5 normal modes, as it is seen in Fig. 6. The second and third peaks, in the RIXS spectrum, are predominantly formed from the first excited vibrational states of the ν_8 and ν_5 modes, respectively, with smaller contributions from the ν_6 and ν_7 modes. The total vibrational progression is made up of $(\nu_8, 0, 0, 0)$ and $(0, 0, 0, \nu_5)$ and both are dressed by mixed excitations, or overtones. At energy loss $\omega - \omega' > 0.5$ eV we observe the formation of a ‘‘tail’’ due to the high density of close-lying vibrational levels corresponding to mixed overtones of different modes.

4. Dynamical origin of splitting of $2a''$ peak

Let us come back to the RIXS via core-excitation to state $8A'$ where methanol dissociates along the normal coordinate $Q \equiv Q_{\nu_1}$ which corresponds to elongation of the OH bond. In Sec. IV B 1, the atomic-like feature^{24,25,58,63} at $\omega - \omega' \approx 8$ eV (Fig. 5) was attributed solely to the transition to the ground state of the product of the dissociation, core-excited methoxy radical CH_3O^* :



However, there is another RIXS channel which also contributes to this feature. The methoxy radical belong to the C_{3v} point group with the doubly degenerate X^2E ground state⁶⁴. This means that two electronic states of methanol should have the same dissociation limit; Namely, the ground state $|GS\rangle = |1A'\rangle$ and the dissociative $|2a''^{-1}8a'^1\rangle$ state (see Fig. 8). Therefore, the atomic-like peak is formed by two RIXS channels: The first one studied in Sec. IV B ends up in the ground state $|GS\rangle$ while the final dissociative valence excited state $|2a''^{-1}8a'^1\rangle$ is the reason for the second RIXS channel. The RIXS profile depends on the PECs of the core-excited and final states. This motivates us to look on the difference of the PECs $\Delta U_{cf}(Q) = U_c(Q) - U_f(Q)$ for final states $|f\rangle = |GS\rangle$ and $|f\rangle = |2a''^{-1}8a'^1\rangle$ (Fig. 8). In this Section we focus on gross features of RIXS, the molecular band and the atomic-like peak, within a 1D model, taking into account only the ν_1 mode. It is well known that the molecular band and the atomic peak strictly coincide with each other when the PECs of core-excited and final states are exactly parallel²⁵. One can see (Fig. 8) that the PEC of the final $|2a''^{-1}8a'^1\rangle$ state is almost parallel to the one of the core-excited state; Contrary to the ground final state. Fig. 8 shows that the region of formation of atomic-like peak, defined by the condition $\Delta U_{cf}(Q) = \text{const}$, starts at $Q \approx 1$ a.u. for the valence final state $|2a''^{-1}8a'^1\rangle$ while for the ground final state it starts for longer distances $Q \gtrsim 3$ a.u.. It takes about 5 fs for the wave packet to reach $Q \approx 1$ a.u. and 10 fs for $Q \approx 3$ a.u.. For quasi-elastic RIXS channel to the ground state, the maxima of atomic-like

peak and maximum of the molecular band are separated by $\omega'_{\text{mol}} - \omega'_{\text{at}} \approx \Delta U_{c0}(0) - U_{c0}(\infty) = 8$ eV (Fig. 8). In contrast, the scattering to the dissociative $|2a''^{-1}8a^1\rangle$ state is expected to have close lying atomic-like and molecular peaks with the spacing of only $\omega'_{\text{mol}} - \omega'_{\text{at}} \approx \Delta U_{cf}(0) - U_{cf}(1a.u.) = 0.95$ eV (Fig. 8). This expectation is nicely confirmed by the simulated RIXS profile (Fig. 9) with $\omega'_{\text{mol}} - \omega'_{\text{at}} = 0.76$ eV. We notice that a similar behaviour has been observed in the water molecule⁶⁵. The nature of the atomic-like peaks arising in the RIXS to the valence-excited and ground states is different. The decays in core excited fragment of dissociation methoxy radical form atomic-like peak when the final state is the ground one. **Contrary to the ground state RIXS channel, where the atomic-like peak is formed at the dissociation limit, the origin of atomic-like peak for the $|2a''^{-1}8a^1\rangle$ RIXS channel is mainly the decay transition in the CH_3OH not far from the equilibrium and its position is rather close to molecular band (Fig. 8, 9).** Due to this, we called it a pseudo-atomic peak.

Results of the 1D simulations of RIXS profile, shown in Fig. 9, demonstrate also the role of isotope substitution. First of all one can see the effect of the isotope substitution on the vibrational progression, simply caused by the difference in OH and OD vibrational frequencies. The second effect we observe is related to the slowdown of the nuclear wave packet in the dissociative core-excited state of CH_3OD in comparison to the CH_3OH because of the heavier deuterium atom. This makes the pseudo-atomic peak in RIXS of CH_3OD less intense than in the CH_3OH in good agreement with the experiment¹⁵ (Fig. 9). There is also another tool to distinguish pseudo-atomic and molecular peaks: The dispersion law. As it is well known^{24,25} the emission energy of the pseudo-atomic peak should not depend on the excitation energy ω contrary to the molecular band which has Raman dispersion (see Fig. 10). One should notice that the role of the ground state RIXS channel in formation of the pseudo-atomic peak near $\omega - \omega' \approx 8$ eV is rather weak in contrast to the region of vibrational progression $0 \leq \omega - \omega' \lesssim 5$ eV (see lower panel in Fig. 11). Similarly to the quasi-elastic channel, shown in Fig. 7, the intensity of the pseudo-atomic peak formed in the inelastic channel (Fig. 10) drops as we tune away from the top of the $8a^1$ XAS resonance. To conclude one should stress that the RIXS channel to $|2a''^{-1}8a^1\rangle$ final state would have only a molecular peak if the nuclear motion was neglected. However, the dissociation of the core excited methanol molecule along the ν_1 PEC of this state results in an additional resonance, the pseudo-atomic peak. Thus the splitting of the $|2a''^{-1}8a^1\rangle$ resonance is dynamical in nature.

Let us turn our attention to the polarization dependence of studied RIXS profile which can be significant due to different orientations of the decay transition dipole moments \mathbf{d}_{c0} and $\mathbf{d}_{2a''}$ to the ground and to the $|2a''^{-1}8a^1\rangle$ states. Indeed, the transition dipole moments \mathbf{d}_{c0} and $\mathbf{d}_{2a''}$ of these channels are orthogonal each other (see Table III) since the the molecular orbital $8a^1$ is lying in the molecular plane while the $2a''$ orbital is orthogonal to this plane because of its π character (Fig. 1). Due to this and eqs. (10), (11) the total RIXS cross-section (9) in the region $\omega - \omega' \lesssim 8$ eV is the sum of two contributions

with different polarization dependence reads

$$\sigma(\omega', \omega) = \frac{d_{c0}^2}{30} [d_{c0}^2 2(2 - \cos^2 \chi) \sigma_0 + d_{2a''}^2 (3 + \cos^2 \chi) \sigma_{2a''}]. \quad (18)$$

The partial cross-sections σ_0 and $\sigma_{2a''}$ corresponding to the RIXS to the ground and $|2a''^{-1}8a^1\rangle$ states, respectively are computed using eq.(9) with $D_{c0} = D_{fc} = 1$ within one-dimensional model (Fig. 8) taking into account only elongation of the OH bond. As expected, the RIXS profile (18), shown in Fig. 11, displays a strong scattering anisotropy for both CH_3OH and CH_3OD .

C. Inelastic X-ray Raman scattering (electronic degrees of freedom)

Response calculations for RIXS transition strengths were performed using the CPP-ADC approach. In this work we limited ourselves to the second-order ADC(2) model for the response calculation. However, we point out that by using higher order models the description of the valence-excited states can be improved as we discuss in a more detailed analysis found in Appendix B. The calculation of RIXS spectra were limited to setting frequencies of the incident field equal to the transition frequencies of the first two absorption peaks in the corresponding XAS spectrum, *i.e.*, 534.29 and 535.46 eV for transitions $a' \rightarrow 8a^1$ and $a' \rightarrow 9a^1$, respectively. The RIXS scattering amplitude matrices were computed for each frequency taking the first 35 valence-excited states in each irreducible representation into account. Based on the scattering amplitudes, RIXS transition strengths were evaluated for different angles (0° , 45° and 90°) between the wave vector of the incident radiation and the propagation vector of the outgoing photon. For the comparison of our simulated spectra with the experimental spectra of Benkert¹⁵ we will start by briefly restating the key elements of our theoretical approach and the experimental assignment.

In our CPP-ADC(2) approach we evaluate the contribution to the RIXS transition strength for each individual final valence-excited state. This results in the stick spectra given in Fig. 12, where the peak heights are defined by the RIXS transition strength for the different angles and the peak positions are defined by the energy loss, *i.e.*, the energy of the incident photons less the respective valence-excitation energy. By including the 35 lowest states in each irreducible representation, we recover all valence-excited states with an excitation energy smaller than 15.5 eV, or, in other words, an emission photon energy of 520 eV. On the technical side, we point out that we chose the aug-cc-pVTZ basis set for this part of our study to avoid artificial valence-Rydberg mixing in the description of the final states in the scattering process. Including more diffuse functions would lead to an artificially higher density of states in the chosen spectral window of 0–15.5 eV. The valence eigenstates are calculated without a lifetime and vibrational broadening in contrast to the intrinsically included lifetime broadening of the core-excited states. Thus, in order to obtain spectra comparable with the experimental ones, a summation of Lorentzian-broadened (broadening of 0.25 eV)

contributions to the RIXS transition strength of each valence-excited final state has been carried out.

The assignment of the spectral features performed by the experimentalists is based on a single-particle picture. In this picture the core-excited state is described by a vacant core orbital (core-hole) and an electron occupying a virtual orbital. Each peak is labeled with a decay transition to the respective core-hole from different occupied orbitals, yielding the final valence-excited state. To 0-th order, these states can be described by single-reference configurations based on the Hartree–Fock orbitals. However, our second-order ADC approach describes both the core- and valence-excited states as correlated states, *i.e.*, as multi-reference configurations. Still, the states are dominated by the 0-th order contribution, which justifies labeling the states by the largest entry in the excitation vector. This labelling makes it possible to compare our simulated spectra to the experimental ones. It should be noted that in the case of ADC the entries of the excitation vector refer to the dynamically correlated basis of the so-called intermediate state representation (ISR), which, again in 0-th order, can be viewed as single-reference states.

The spectra in Fig. 12, resulting at the resonance frequency of the first core-excited state, show five main peaks. The peak-labels for the spectrum of the $8\mathcal{A}'$ state refer to the valence-excited state with the largest RIXS transition strength under the respective peak. In addition, the largest entry in the excitation vector is given for each state. The assignment based on the excitation vectors is in agreement with the that performed by the experimentalists. For the spectra of the second core-excited state the transitions corresponding to the same valence-occupied orbitals are shifted to higher energies, again agreeing with experiment.

To discuss the details of the simulated spectra, we look at the contributions from the two lowest valence-excited states $1A''$ and $2A''$. The largest peak in the lower panel of Fig. 12 originates from the $1A''$ state and corresponds to a relaxation of the first core-excited state $8\mathcal{A}'$ in terms of filling the $1a'$ core-hole with an electron from the $2a''$ valence orbital. Less intuitively, the same valence state also gives rise to a peak in the RIXS spectrum in resonance with the second core-excited state $9\mathcal{A}'$; in this case it appears as a **shoulder blue-shifted with respect to the $2A''$ peak**. This shoulder peak has two qualitatively different contributions of comparable sizes. The first contribution is due to the multi-reference nature of the involved states. As a result, the valence $1A''$ state is coupled to the second core-excited state and shows a non-zero transition-dipole moment despite the fact that the 0th order wave functions differ in occupation by a two-electron excitation. The second contribution, which is even more important in this case and gives rise to the majority the intensity of the $1A''$ in the upper part of Fig. 12, is due to nonresonant inelastic scattering. The nonresonant contribution at the frequency of the $9\mathcal{A}'$ state originates, for example, from weak nonresonant population of the $8\mathcal{A}'$ core-excited state followed by strong decay to the $1A''$ final state. The nonresonant scattering channel contributes to the real components of the scattering amplitude matrix, which are larger than the imaginary resonant contributions at the same frequency for the $1A''$ state. Like-

wise for the $2A''$ state, it appears as a strong peak in the spectrum at the frequency in resonance with the $9\mathcal{A}'$ state but only as a weak spectral feature at the frequency in resonance with the $8\mathcal{A}'$ state. We emphasize that a quantitative description of this nonresonant inelastic scattering effect is only achieved by including the full summation in the Kramers-Heisenberg expression²⁵.

Overall, a large number of valence-excited states contribute to the spectral shape. This leads to additional features, especially for the second core-excited state in the region between the peaks of the $7a' \rightarrow 9a'$ and $5a' \rightarrow 9a'$ transitions. Here the additional peaks besides those originating from the $1a''$ and the $6a'$ orbitals, stem from transition with significant Rydberg-character. The higher density of states in the high valence-energy region (lower emission photon energy) can be understood as a consequence of a growing number of possible configurations in the mixing of the states involving higher-lying unoccupied orbitals with increasingly diffuse character.

The first RIXS transition $2a'' \rightarrow 1s_O$ deserves a special comment. Contrary to transitions from another MOs the peak position of this resonance is almost insensitive to the intermediate core-excited state. Indeed, the spacing between the RIXS peaks for final states $2a'' \rightarrow 8a'$ and $2a'' \rightarrow 9a'$ is very small, 0.088 eV (see Fig. 12). The reason for this is the non-bonding character of the $2a''$ orbital which behaves rather similarly to the $1s_O$ orbital (like the $1b_1$ orbital in H_2O molecule⁴⁴). This makes the $2a'' \rightarrow 1s_O$ transition very special in RIXS of liquid methanol (see Sec. IV D) and similar to the $1b_1 \rightarrow 1s_O$ transition in liquid water^{2,3,66}.

Finally, we look at the angular dependence of the RIXS profile in Fig. 12. To understand this dependence one should look at Eq. (11), assuming for simplicity that $(\hat{\mathbf{d}}_{\mathcal{A}'} \cdot \hat{\mathbf{d}}_{A'})^2 = 1$,

$$\sigma_{\mathcal{A}'A''} \propto 3 + \cos^2 \chi, \quad \sigma_{\mathcal{A}'A'} \propto 2 - \cos^2 \chi. \quad (19)$$

Here, the first channel $\sigma_{\mathcal{A}'A''}$ corresponds to the peaks $2a'' \rightarrow 8a'$ and $2a'' \rightarrow 9a'$ while the peaks $7a' \rightarrow 8a'$ and $7a' \rightarrow 9a'$ are described by the cross section $\sigma_{\mathcal{A}'A'}$ in Fig. 12. In agreement with Eq. (19), the RIXS peaks $2a'' \rightarrow na'$ and $7a' \rightarrow na'$ display opposite dependence on the angle $\chi = \angle(\mathbf{e}, \mathbf{k}')$.

D. Aspects of RIXS from liquid methanol

The understanding of the formation of the RIXS spectrum of gas phase methanol provides a robust foundation to shed light on RIXS of methanol in liquid phase. The quasi-elastic RIXS differs qualitatively from electronically inelastic resonant X-ray scattering. This type of RIXS shows nicely resolved vibrational structure in different aggregate states of matter: crystalline and amorphous solids⁶⁷, liquid acetone⁶² and water^{3,68,69}. RIXS experiments have been performed at the ADDRESS - X03MA beamline⁷⁰ at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland, using the SAXES spectrometer⁷¹ with a combined spectral resolution of 50-60 meV in our measurements. Liquid samples were prepared in a flow-cell with a 150 nm thick Si_3N_4 window coated with 10 nm gold on the inside. The sample in the interaction

region was renewed during the measurements. Linearly polarized X-rays were used with the polarization vector perpendicular to the scattering plane defined by the incident x-ray beam and the direction of detection. The energy calibration was based on the vibrationally resolved O₂ spectrum⁷². These new measurements with much better resolution in comparison with the earlier experiment¹² nicely resolve vibrational structure of RIXS as it is shown in Fig. 13 for the photon energy tuned in the resonance with the pre-edge peak of the OK XAS. The **raw** experimental RIXS spectrum contained two symmetric artefacts due to X-ray optics at approximately ± 0.65 eV with respect to the elastic line. This artefact, presented as an isolated peak on the red side of the spectrum, was mirror reflected to the blue part of the spectrum and subtracted from **the raw data to generate the artefact-free spectrum shown in Fig. 13**.

Although our simulations are performed for free methanol molecules, the comparison of the simulations with the experiment for liquid methanol shows that the gas phase quasi-elastic RIXS is rather similar to the RIXS of liquid phase. The experimental quasi-elastic RIXS of liquid methanol display the OH vibrational progression with a vibrational frequency of $\omega_{v_1} = 0.425$ eV which is rather close to the experimental IR frequency $\omega_{v_1} = 0.456$ eV (see Table I). One can see that the vibrational progression in liquid phase is significantly shorter than in gas phase methanol. The reason for this is the strong fluctuation of outermost part of the OH potential due to fluctuation of the hydrogen bond network. This results in a randomization of the high energy part of the RIXS spectrum of liquid methanol similar to the RIXS of liquid water³ and, hence, in a shortening of the vibrational progression in RIXS of liquid methanol (Fig. 13). The fine structure seen in the simulated gas phase RIXS profile (Fig. 5) is washed out in liquid phase (Fig. 13) due to the broadening of the vibrational resonances by much weaker fluctuation of the OH potential in inner region.

Let us turn our attention to the split $2a''$ RIXS peak discussed in Sec IV B 4. Similar splitting, observed in the RIXS spectra of liquid methanol¹², has been debated. There are two distinct interpretations of the origin of this splitting - a dynamical¹² and a structural interpretation⁷³. Both interpretations use a model based on double-well potentials for core-excited and final states⁷⁴ which are applicable only for the Rydberg core-excitation or core-ionization of the methanol-dimer. Here we focus only on the pre-edge core-excitation to the dissociative state which we studied in Sec. IV B 4 for the gas phase. As one can see from Fig. 11, the main contribution to the region around the $2a''$ RIXS band comes from the RIXS to the dissociative valence $|2a''^{-1}8a''^1\rangle$ excited state. As it was already explained in Sec. IV B 4 (see also Fig. 8), the formation of the split $2a''$ peak comes from the decay transitions in core-excited CH₃OH in the range rather close to the equilibrium $Q - Q_0 \lesssim 1$ a.u. where the role of hydrogen bond network is expected to be weak similar to liquid water³. Here it is important to remind that the $2a''$ orbital being non-bonding is rather similar to the non-bonding $1s_O$ orbital (see also Sec. IV C). Akin to the $1b_1 \rightarrow 1s_O$ transition in liquid water the parallelism of the potentials of the $|2a''^{-1}8a''\rangle$

and $|1s_O^{-1}8a''\rangle$ states is preserved even for longer distances, $Q - Q_0 \gtrsim 1$ a.u.⁷⁵. This clearly shows that the nature of the splitting of the $2a''$ peak in liquid is the same as in gas phase methanol at least for pre-edge core excitation. The same excitation energy dependence of the RIXS of liquid and gas phase methanol, in the region near the pseudo-atomic peak (Fig. 14), is another evidence of the dynamical origin of the splitting of the $2a''$ peak. Indeed, both liquid and gas phase spectra display Raman dispersion of the molecular band contrary to the pseudo-atomic peak whose peak position does not depend on the excitation energy²⁵.

The experiment shows a structure on the low energy side of the pseudo-atomic peak which is absent in the theoretical spectrum. This can be due to contributions from other vibrational modes, similar to the RIXS of H₂O⁶⁵, that are ignored in the 1D calculations presented in Fig. 14. The theoretical spectrum shows another interesting feature, seen for $\omega < 534.5$ eV, namely the gradual transformation of the pseudo-atomic peak into the interference hole^{24,76}.

V. CONCLUSIONS

We have presented *ab initio* simulations of the X-ray absorption and the resonant inelastic X-ray scattering spectra of gas phase methanol near the oxygen K-edge taking into account the nuclear degrees of freedom. The electronic transitions are calculated using the ADC(2)-x, RASPT2 and TDDFT methods. The multimode nuclear motion is described in the framework of a “mixed representation” where the dissociative states and highly excited vibrational modes are efficiently treated with a time-dependent wave packet technique while the remaining active modes are described using Franck-Condon amplitudes. It is found that multimode nuclear dynamics is of crucial importance for explaining the experimental XAS and available RIXS spectra. The computed XAS spectra clearly illustrate the state-specific vibrational broadening. The reason for this is the different shapes of the potential energy surfaces for different electronic states. The dissociation of the methanol molecule along the OH bond in the first core-excited state, similar to gas phase and liquid water^{2,3}, results in a long vibrational progression in the case of RIXS to the ground state. The ground and dissociative $|2a''^{-1}8a''^1\rangle$ final states have the same dissociation limit. Although both these channels participate in the formation of the pseudo-atomic peak, the main contribution comes from the $|2a''^{-1}8a''^1\rangle$ channel. We have found that the reason for the splitting of the $2a''$ RIXS peak is the slight difference in the dissociative potential of core- and valence-excited final states along the OH bond. This explains the dependence of the shape of the splitted $2a''$ peak on the excitation energy and on the isotopic substitution. We also pay special attention to the polarization dependence of the RIXS profile. The presented *ab initio* simulations quantitatively describe the available XAS¹³⁻¹⁵ and RIXS¹⁵ experimental data. We show the dynamical origin of the splitting of the $2a''$ peak in RIXS of liquid methanol at least for pre-edge core excitation.

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Appendix A: Potential energy curves of inactive modes

As one can see from Fig. 15 the PECs of core-excited states for the remaining modes $v_2, v_3, v_4, v_9, v_{10}$ and v_{11} are almost parallel to the ground state PECs. Hence, these modes are deemed essentially inactive and are excluded in our simulations.

Appendix B: High-level calculations of the excited states energies

The calculations of the RIXS spectra for a broad emission energy range (Fig. 12) were performed at the CPP-ADC(2)/aug-cc-pVTZ level of theory, providing a rather good agreement with the experimental spectra¹⁵ at affordable computational costs. However, the energies and thereby the relative peak positions of the valence-excited states may be further improved by using the higher order ADC(3) method and larger basis sets. The energies and oscillator strengths for several lowest valence-excited states computed using different methods and basis sets are collected in Table IV. The same analysis for several lowest core-excited states is presented in Table V. One can see, that even though the absolute energies could be worse at the level of ADC(3) as compared to experimental one, the relative energy difference is improved. E.g., the energy difference between $1A''$ and $3A'$ states is 2.05 eV at the ADC(2)/aug-cc-pVTZ level, while ADC(3)/d-aug-cc-pVTZ provides a value 1.90 eV, which is closer to the experimental result.

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TABLE I. Experimental³⁰ and theoretical (DFT) frequencies of vibrational modes of methanol in the ground state.

Vibrational mode	Sym.	Exp., cm ⁻¹ (eV)	Theor. (DFT), cm ⁻¹ (eV)	Theor. (CASPT2), cm ⁻¹ (eV)
Torsion	ν_{12} A'	295 (0.036)	296 (0.037)	301 (0.037)
CO stretching	ν_8 A'	1033 (0.128)	1039 (0.129)	1060 (0.131)
CH ₃ rock	ν_7 A'	1060 (0.131)	1076 (0.133)	1093 (0.136)
CH ₃ rock	ν_{11} A''	1165 (0.144)	1170 (0.145)	1188 (0.147)
OH bending	ν_6 A'	1345 (0.167)	1365 (0.169)	1375 (0.170)
CH ₃ s-deform.	ν_5 A'	1455 (0.180)	1477 (0.183)	1492 (0.185)
CH bending	ν_{10} A''	1465 (0.182)	1498 (0.186)	1523 (0.188)
CH bending	ν_4 A'	1477 (0.183)	1508 (0.187)	1533 (0.190)
CH stretching	ν_3 A'	2844 (0.353)	2994 (0.371)	3054 (0.378)
CH stretching	ν_9 A''	2960 (0.367)	3040 (0.377)	3131 (0.388)
CH ₃ d-stretching	ν_2 A'	3000 (0.372)	3109 (0.385)	3189 (0.395)
OH stretching	ν_1 A'	3681 (0.456)	3829 (0.475)	3874 (0.480)

TABLE II. Vertical transition energies (eV) (oscillatory strengths, $f \times 10^{+3}$) of O($1s^{-1}$) core-excitation from RASPT2, ADC(2)-x and REW-TDDFT simulations (see Sec. III for details).

	$8a'$	$9a'$	$3a''$	$10a'$	$11a'$	$12a'$
RASPT2	535.04 (9.56)	536.59 (2.83)	537.10 (0.82)	537.11 (1.51)	537.62 (2.36)	537.85 (4.46)
ADC(2)-x	533.05 (8.97)	534.82 (3.23)	535.14 (2.31)	535.15 (1.26)	535.68 (3.35)	535.97 (5.07)
REW-TDDFT	519.34 (7.61)	521.17 (2.86)	521.47 (4.23)	521.56 (1.94)	522.16 (7.82)	522.48 (6.22)
	$4a''$	$13a'$	$14a'$	$5a''$	$15a'$	$6a''$
RASPT2	538.02 (0.11)	—	—	—	—	—
ADC(2)-x	536.13 (0.001)	536.15 (4.71)	536.23 (1.42)	536.25 (0.23)	536.35 (1.91)	536.51 (0.02)
REW-TDDFT	523.08 (3.92)	523.23 (3.81)	523.45 (2.69)	523.46 (0.90)	523.60 (11.63)	524.05 (7.57)
	$7a''$	$8a''$	$9a''$	$10a''$		
ADC(2)-x	537.31 (0.89)	537.37 (0.69)	537.45 (0.11)	537.62 (0.1)		
REW-TDDFT	524.38 (1.83)	524.39 (5.13)	525.29 (0.56)	526.24 (0.41)		

TABLE III. Components of the transition dipole moments (in a.u.) from RASPT2 calculations in the frame shown in Fig. 1.

Transition	d_x	d_y	d_z	$d= \mathbf{d} $
GS \rightarrow $ 1s_O^{-1}8a'^1\rangle$	-0.00817	-0.03040	0.00000	$d_{c0}=0.03148$
$ 1s_O^{-1}8a'^1\rangle \rightarrow 2a''^{-1}8a'^1\rangle$	0.00000	0.00000	-0.05519	$d_{2a''}=0.05519$

TABLE IV. Valence excitation energies ΔE (eV) and oscillator strength f for methanol, calculated using ADC(2), ADC(2)-x, and ADC(3) methods with the Dunning's basis sets: aug-cc-pVTZ (aTZ), d-aug-cc-pVTZ (dTZ), and t-aug-cc-pVTZ (tTZ)⁴⁵.

		$1A''$		$2A''$		$2A'$		$3A''$		$3A'$	
		$2a'' \rightarrow 8a'$	$2a'' \rightarrow 9a'$	$2a'' \rightarrow 3a''$	$2a'' \rightarrow 10a'$	$7a' \rightarrow 8a'$	ΔE	$f \times 10^3$	ΔE	$f \times 10^3$	ΔE
ADC(2)	aTZ	6.48	4.04	7.57	26.93	8.02	28.10	8.15	6.81	8.53	2.85
	dTZ	6.47	3.70	7.55	24.88	7.90	21.28	7.96	5.35	8.52	2.51
	tTZ	6.47	3.70	7.54	24.86	7.90	21.14	7.96	5.42	8.52	2.49
ADC(2)-x	aTZ	6.11	4.08	7.26	26.43	7.77	29.33	7.87	6.52	8.14	2.43
	dTZ	6.10	3.78	7.24	25.02	7.67	23.35	7.72	5.69	8.14	2.33
	tTZ	6.10	3.78	7.24	25.01	7.67	23.25	7.72	5.74	8.14	2.33
ADC(3)	aTZ	7.15	3.43	8.37	38.24	8.95	38.45	8.98	6.41	9.06	0.21
	dTZ	7.15	3.19	8.36	36.35	8.85	30.46	8.84	5.69	9.06	0.21
Exp. ⁷⁷		6.67		7.83		—		—		8.43	
Exp. ⁷⁸		6.76		7.73		8.31		8.31		—	

TABLE V. Core-valence excitation energies ΔE (eV) and oscillator strength f for oxygen K -edge of methanol, calculated using CVS-ADC(2), CVS-ADC(2)-x, and CVS-ADC(3) methods with Dunning's basis sets aug-cc-pVTZ (aTZ), d-aug-cc-pVTZ (dTZ), t-aug-cc-pVTZ (tTZ)⁴⁵.

	$8s'$		$9s'$		$3s''$		$10s'$		$11s'$	
	$1a' \rightarrow 8a'$		$1a' \rightarrow 9a'$		$1a' \rightarrow 3a''$		$1a' \rightarrow 10a'$		$1a' \rightarrow 11a'$	
	ΔE	$f \times 10^3$	ΔE	$f \times 10^3$	ΔE	$f \times 10^3$	ΔE	$f \times 10^3$	ΔE	$f \times 10^3$
ADC(2)										
aTZ	534.83	5.36	535.99	1.54	536.37	0.37	536.51	0.37	537.16	2.94
dTZ	534.81	5.31	535.93	1.40	536.17	0.48	536.22	0.46	536.60	1.21
tTZ	534.81	5.31	535.93	1.39	536.17	0.48	536.21	0.45	536.59	1.16
ADC(2)-x										
aTZ	533.06	8.94	534.85	3.37	535.32	1.02	535.34	3.02	535.93	5.93
dTZ	533.05	8.97	534.82	3.24	535.16	1.27	535.15	2.31	535.68	3.35
tTZ	533.05	8.97	534.82	3.24	535.16	1.26	535.14	2.30	535.67	3.35
ADC(3)										
aTZ	539.15	20.26	541.24	36.97	542.38	5.11	542.02	7.56	542.69	8.20
dTZ	539.14	20.28	541.23	36.76	542.19	5.23	541.93	6.65	542.52	7.36
tTZ	539.14	20.28	541.23	36.77	542.18	5.22	541.93	6.65	542.52	7.33
Exp. ¹⁴	534.12		535.83		536.32		536.32		537.10	

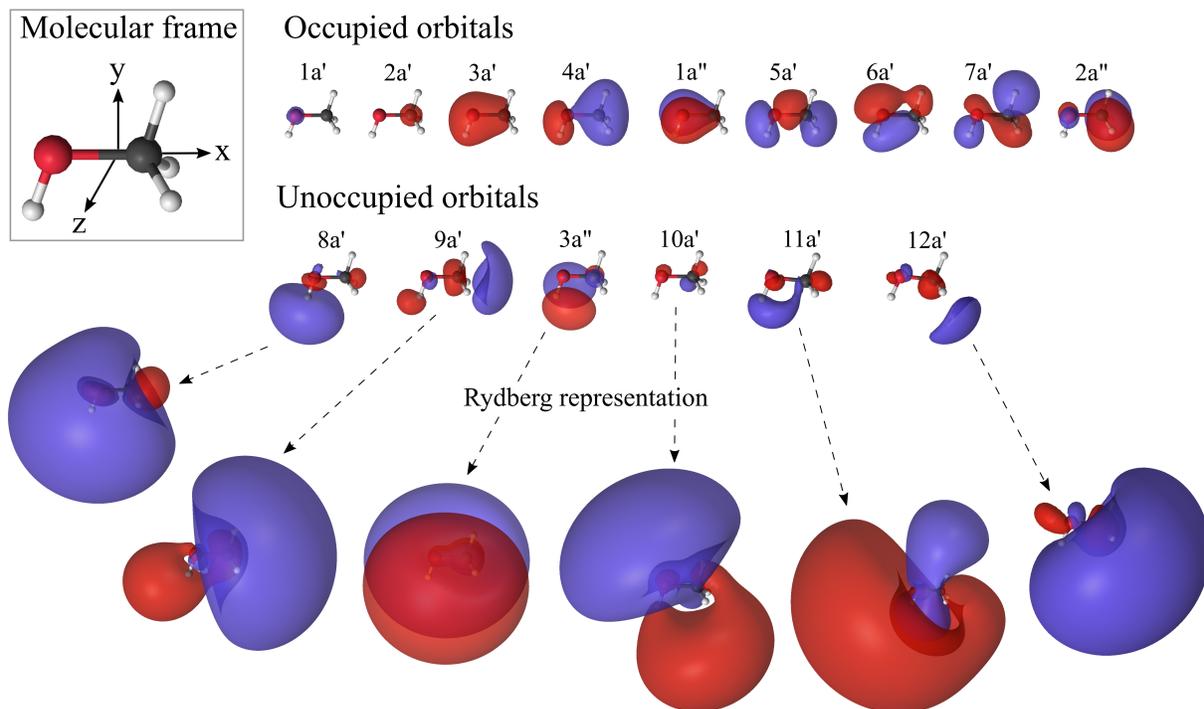


FIG. 1. Occupied natural orbitals are extracted from the ground state multi-electron wavefunction. Unoccupied natural orbitals are extracted from the corresponding state-specific RASSCF calculations of the core-excited states of A' and A'' symmetry. The coordinate system in the molecular frame is shown in the inset of the figure.

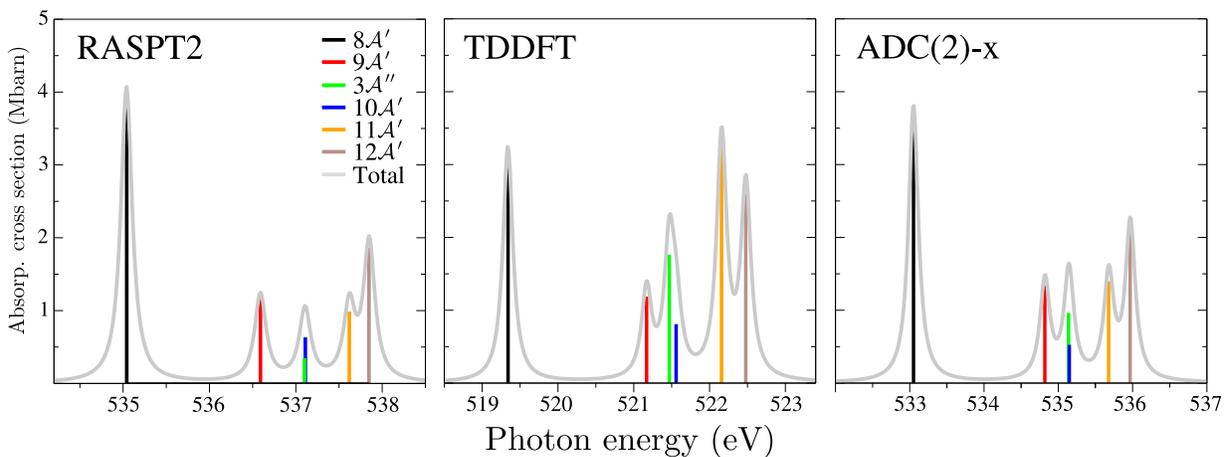


FIG. 2. XAS of gas-phase methanol at O K-edge, neglecting nuclear motion, with three different methods: RASPT2 (left), TDDFT (middle), and ADC(2)-x (right). Absorption cross sections for each state are shown with the bars of correspondent colour (see legends), the total spectra is obtained by the convolution with the spectral function of half-width at half maximum $\Gamma = 0.08$ eV, accounting for the lifetime broadening.

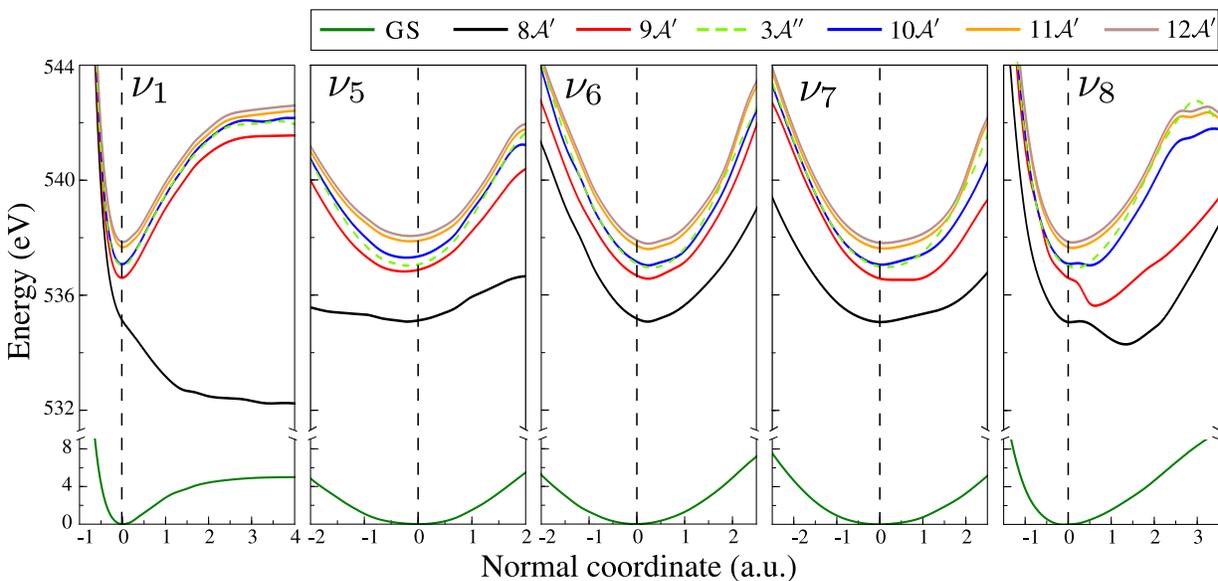


FIG. 3. Potential energy curves along the five most active vibrational modes computed at the RASPT2 level of theory. The ground state (solid green line) and seven lowest core-excited states (see legends for assignment) are shown. Vertical dashed lines show the equilibrium geometry of each mode.

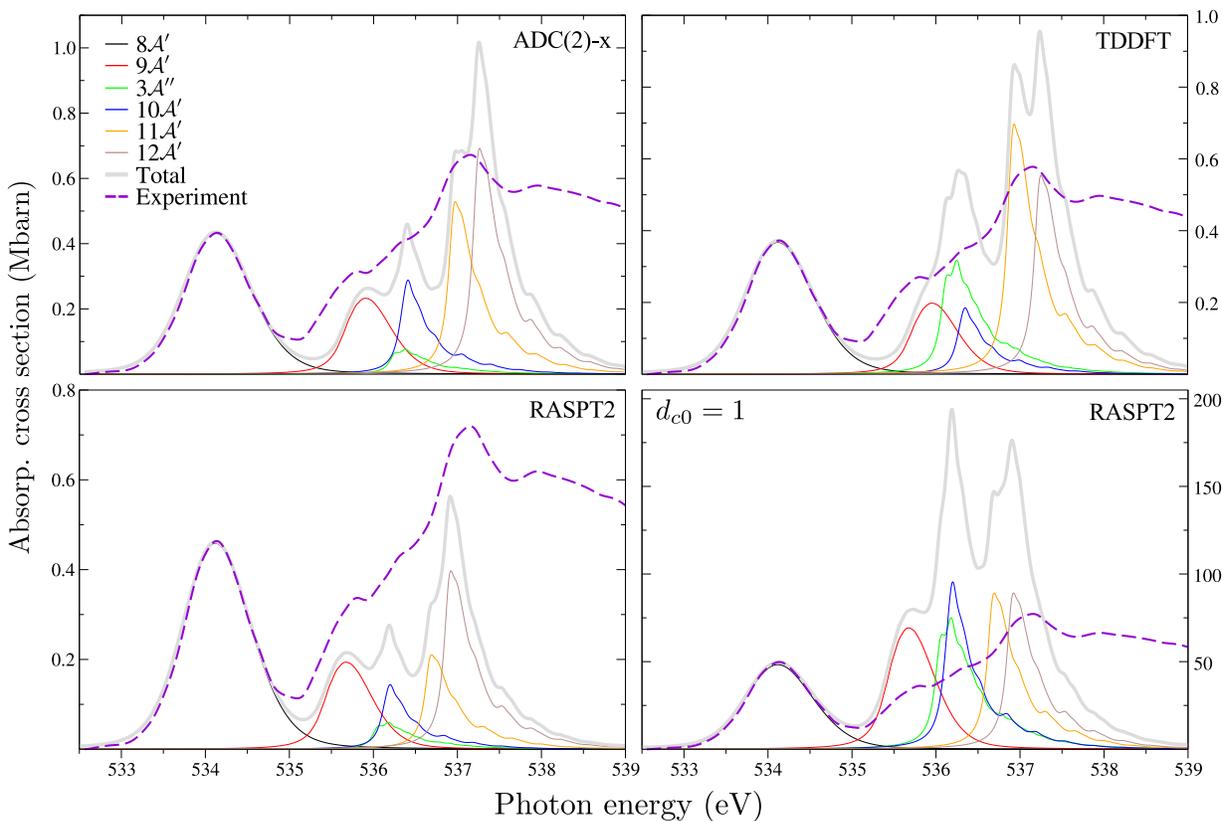


FIG. 4. XAS spectrum of gas phase of methanol at O K edge taking into account nuclear motion compared to experiment¹⁴. To focus on the intensity distribution of XAS the theoretical profiles are shifted to match the first experimental peak $8A'$. The actual transition energy of the first peak for each theoretical method is given in Table II. **The lower right panel shows a hypothetical absorption spectrum where the electronic transition dipole moments are set to one, to isolate the purely vibrational contributions.**

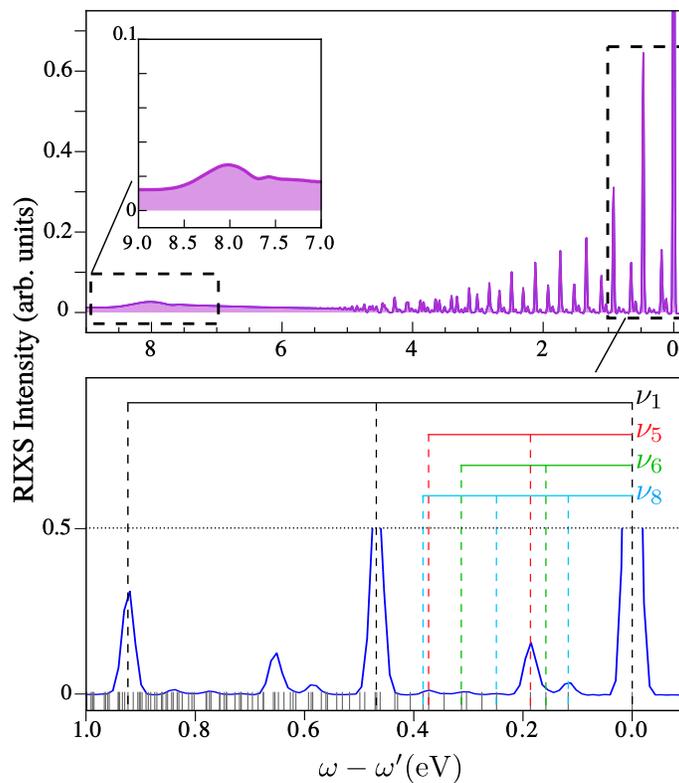


FIG. 5. Profile of quasi-elastic RIXS. Photon energy is tuned in resonance with dissociative $|1a'^{-1}8a'^1\rangle$ core-excited state. The lower panel shows a zoom of the RIXS spectrum in the region $[-0.1$ to 1.0 eV] with assignment of the main vibrational progressions of the ν_1 , ν_5 , ν_6 , and ν_8 modes. The black bars illustrate all possible vibrational overtones of these modes.

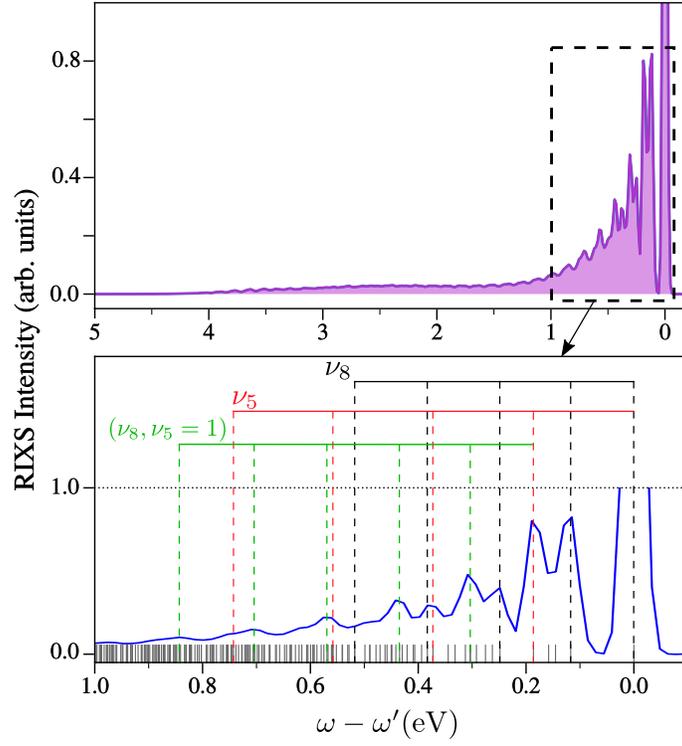


FIG. 6. Profile of quasi-elastic RIXS. Photon energy is tuned in resonance with bound $|1a'^{-1}9a'^1\rangle$ core-excited state. The lower panel shows a zoom of the RIXS spectrum in the region $[-0.1$ to 1.0 eV] with assignment of the two main vibrational progressions of the ν_8 and ν_5 modes, as well as an overtone progression $(\nu_8, \nu_5 = 1)$ given its significant contribution to the spectrum. The black bars illustrate all possible vibrational overtones of the four modes $\nu_5, \nu_6, \nu_7,$ and ν_8 taken into account.

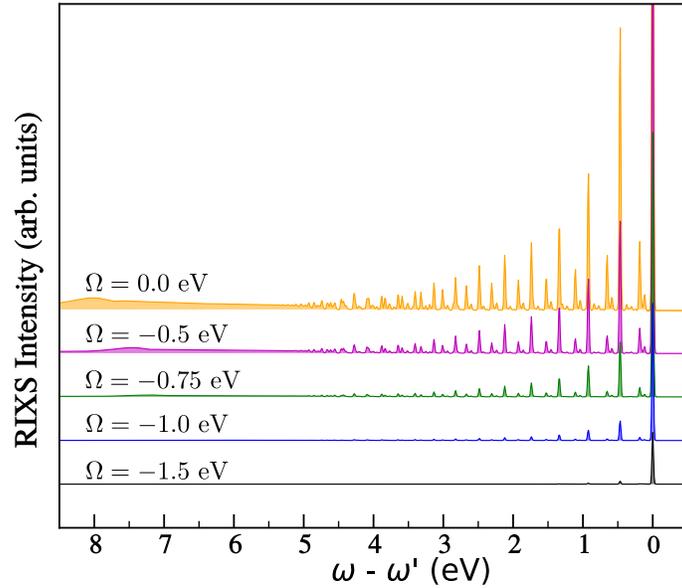


FIG. 7. Dependence of the RIXS profile on the detuning Ω near the first core-excited state $|1a'^{-1}8a'^1\rangle$, which illustrates the collapse of the vibrational progression at large values of Ω due to decrease of the effective scattering duration time τ , see (15).

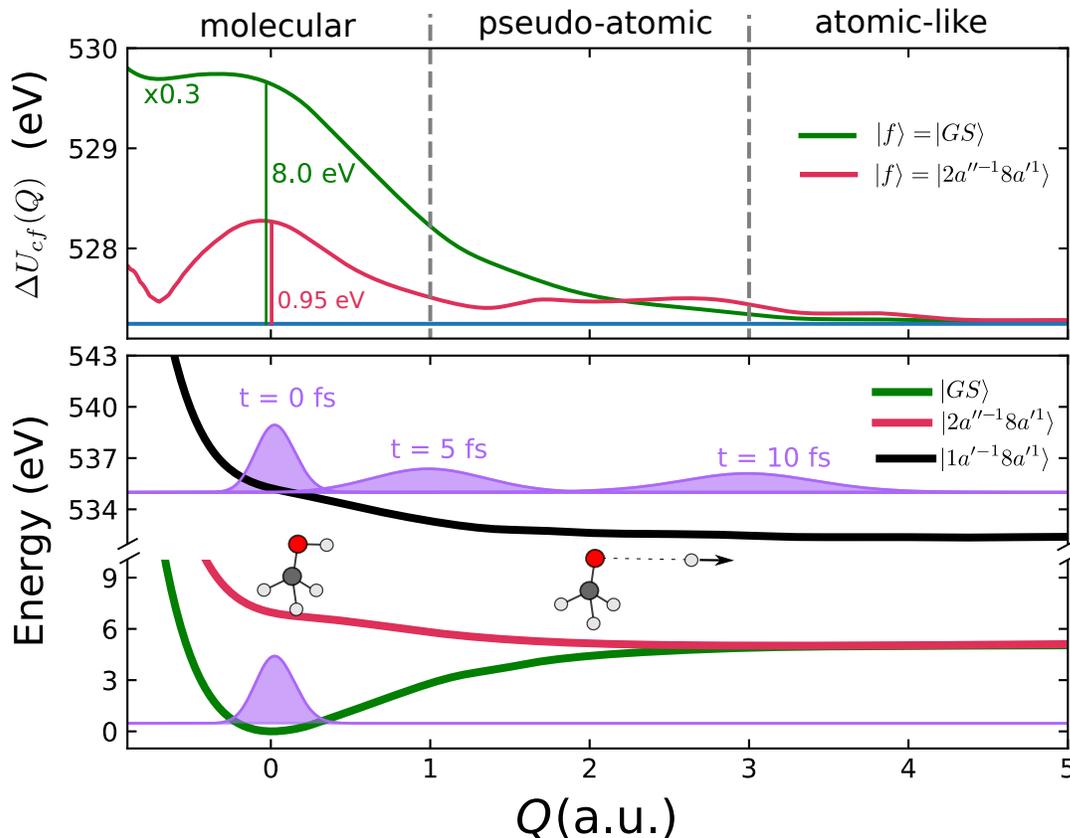


FIG. 8. Potential energy curves for the ground, core-excited $8a'$ and final dissociative $|2a''-18a'1\rangle$ states together with the evolution in core excited state of square of nuclear wave packet, $|\psi_c(t)|^2$ (lower plot). Functions $\Delta U_{cf}(Q) = U_c(Q) - U_f(Q)$ (lower plot) for the ground (green line) and the first valence excited (red line) states show the transition emission energy at distance Q . Approximately divided regions of formation of the molecular band, pseudo-atomic and atomic-like peaks are labeled on the top of the upper plot.

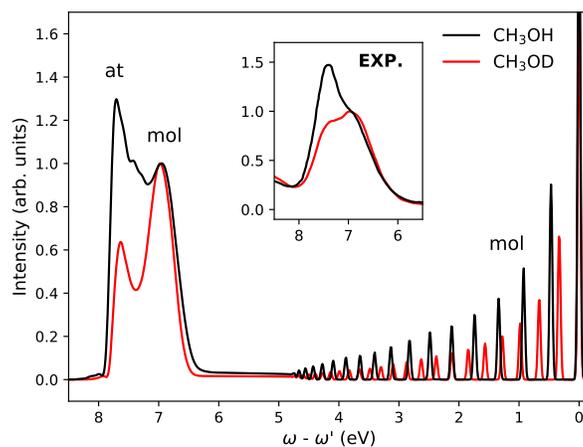


FIG. 9. Role of the isotope substitution. Full profile including pseudo-atomic peak: MeOH vs MeOD. $\chi = 90^\circ$. The spacing between the pseudo-atomic peak (at) at and maximum of the molecular band (mol) is equal 7.71 eV and 0.76 eV for the RIXS channel which ends up in the ground state and in the $|2a''-18a'1\rangle$ valence excited state, respectively. The inset shows correspondent experimental spectra taken from ref.¹⁵.

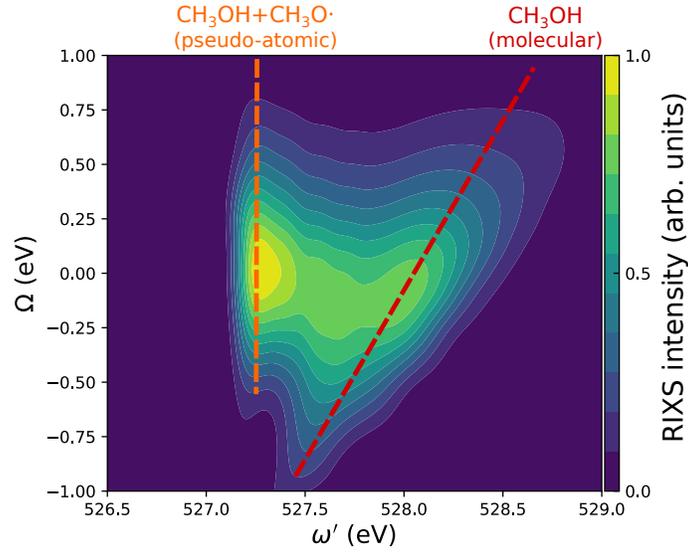


FIG. 10. RIXS map of the $|2a''^{-1}8a'^1\rangle$ peak: the vertical axis shows excitation energy as detuning $\Omega = \omega - \omega_{\text{op}}$ from the top of the lowest core-excited resonance $|1a'^{-1}8a'^1\rangle$, the horizontal axis corresponds to the RIXS emission energy. The position of the pseudo-atomic peak (decay both in CH_3OH and $\text{CH}_3\text{O}\cdot$) does not depend on the excitation energy ω contrary to the molecular band (decay in CH_3OH) which follows the Raman law.

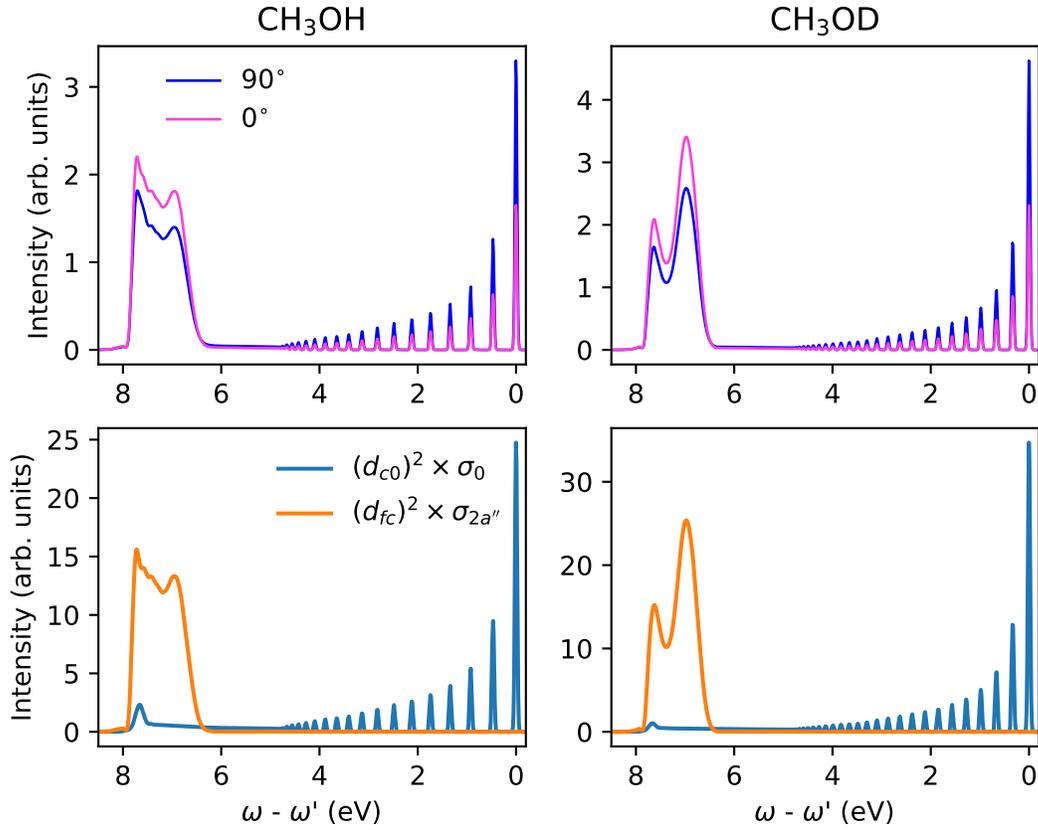


FIG. 11. RIXS via the lowest core-excited state $|1a'^{-1}8a'^1\rangle$ for CH_3OH (left panels) and CH_3OD (right panels). Upper panels display the polarization dependence of the RIXS cross sections, where $\chi = \angle(\mathbf{e}, \mathbf{k}') = 0^\circ$ and 90° (see 111legend). The lower panels show the partial contributions to the RIXS cross section (18) from the scattering channels to the ground state (blue line) and to the lowest valence excited state $|2a''^{-1}8a'^1\rangle$ (orange line).

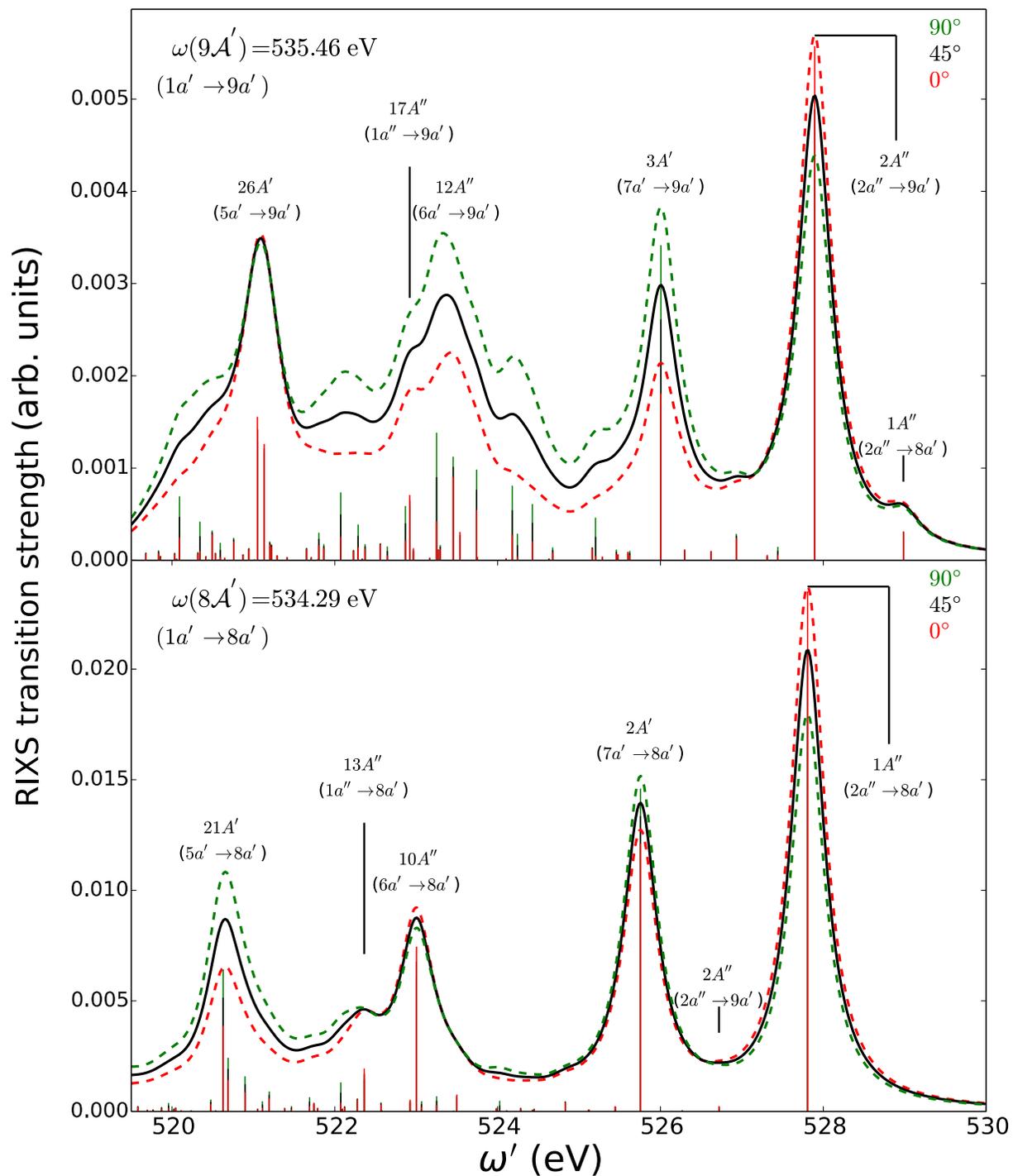


FIG. 12. RIXS spectra of methanol via the two lowest core-excited states $|1a'^{-1}8a'^1\rangle$ (lower panel) and $|1a'^{-1}9a'^1\rangle$ (upper panel) simulated at the CPP-ADC(2)/aug-cc-pVTZ level of theory. Angular dependence is shown for $\chi = 0^\circ$, 45° , and 90° with red, black, and green curves, respectively. The sticks represent the contribution of individual final states to the RIXS transition strength, the assignment of the main contributions based on one electron transitions is given next to each peak. The curves have been obtained by summing up Lorentzian-broadened (broadening 0.25 eV) contributions.

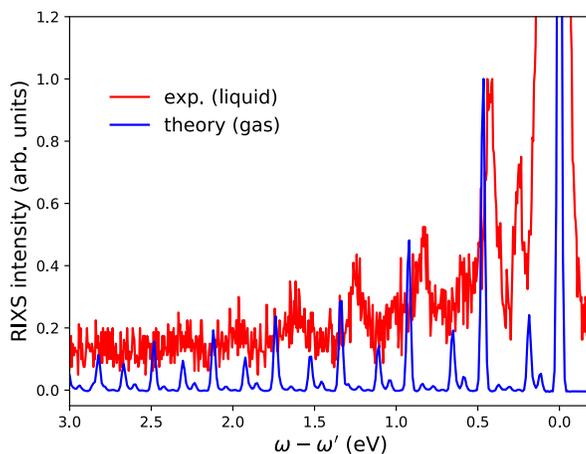


FIG. 13. Comparison of experimental RIXS of liquid methanol with the theoretical multimode RIXS profile of gas phase methanol from Fig. 5. The deviation of the theoretical (gas) vibrational progression from the experimental one (liquid) is due to two reasons. The first one is the intrinsic difference of vibrations in gas and liquid while the second one is the limitation of the theoretical model used. The photon frequency was tuned in the experiment in the pre-edge region $\omega = 534.5$ eV.

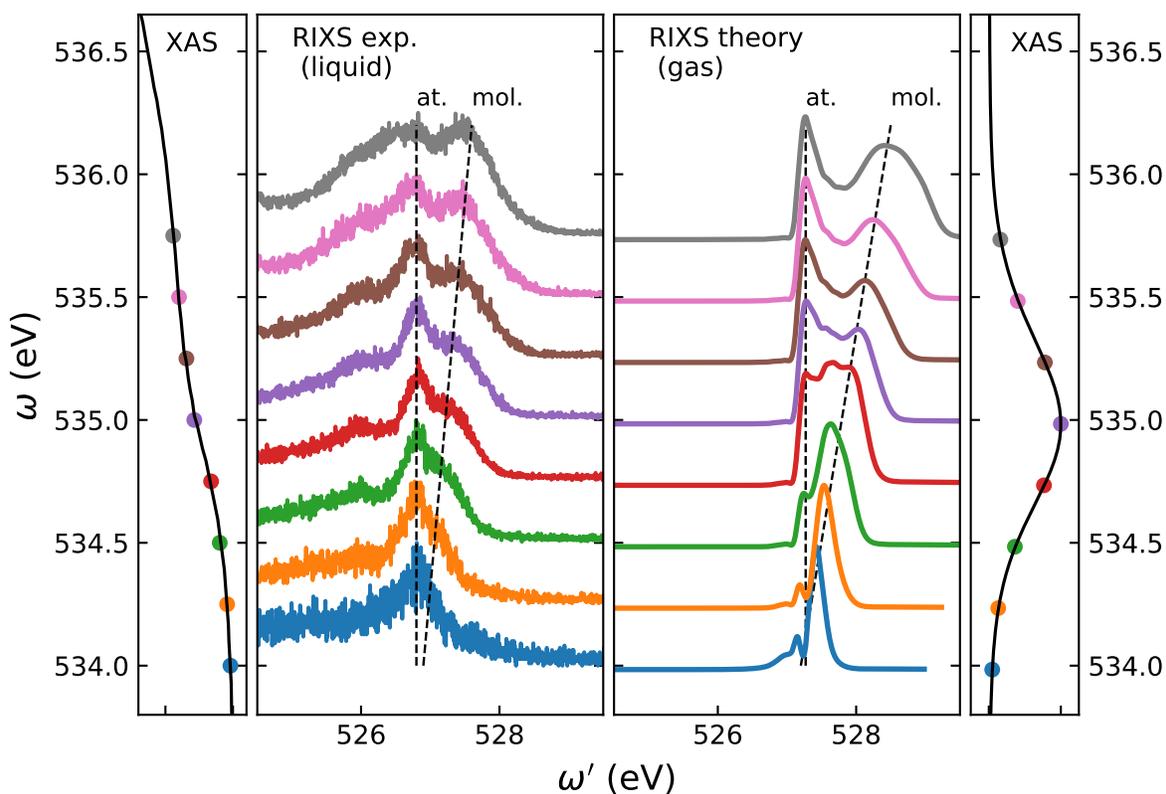


FIG. 14. Comparison of the excitation energy dependence of the experimental RIXS of liquid methanol with the theoretical single-mode RIXS profile of gas phase methanol in the region of the $2a''$ peak (see Fig. 9 for the whole RIXS map). Both liquid and gas phase spectra display nondispersive character of the pseudo-atomic peak and Raman dispersion of the molecular band. The coloured circles show the correspondence of the RIXS profile and the excitation energy ω .

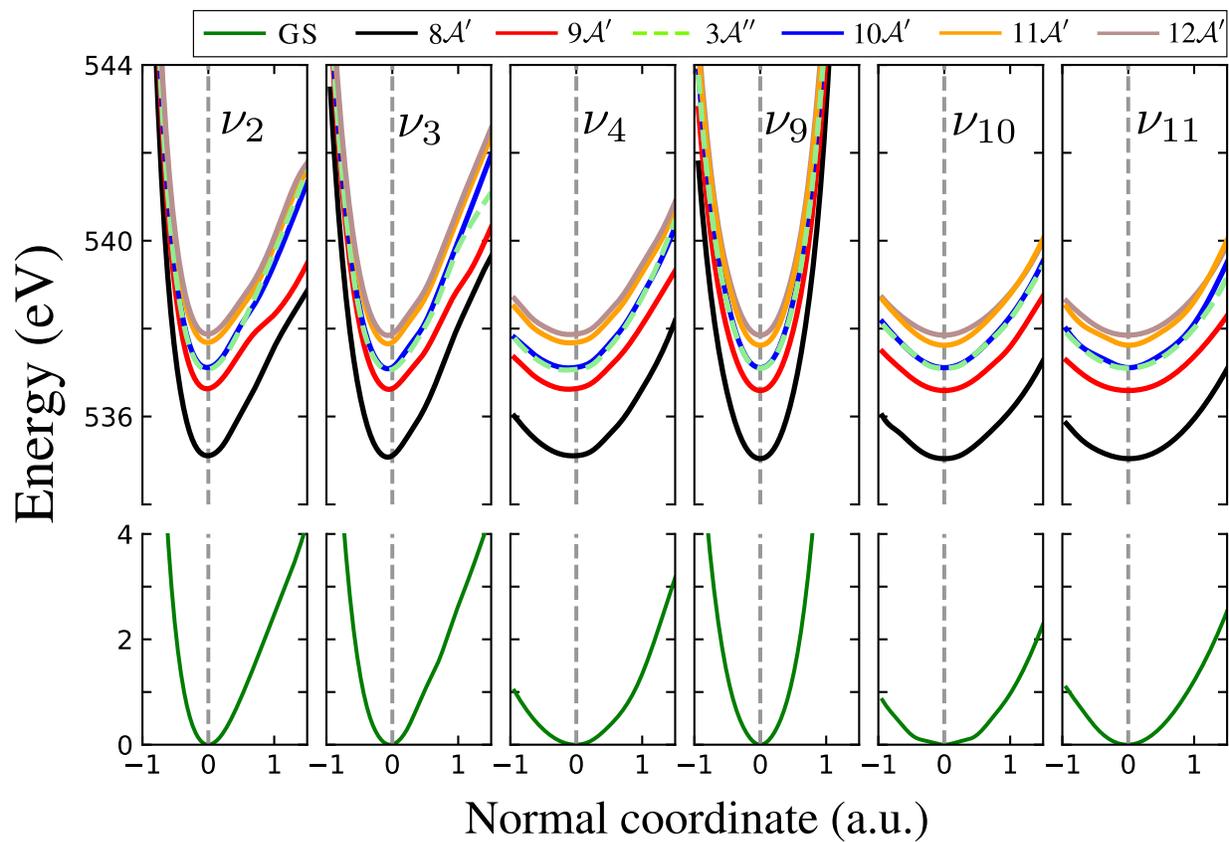


FIG. 15. Potential energy curves for the vibrational modes not taken into account in our simulations. Contrary to the active modes (Fig. 3), those shown in the present figure are not active because the PECs of core-excited states are not shifted with respect to the ground state PECs (green lines).