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

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ABSTRACT
We report on a combined theoretical and experimental study of core-excitation spectra of gas and liquid phase methanol as obtained with the use of X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS). The electronic transitions are studied with computational methods that include strict and extended second-order algebraic diagrammatic construction [ADC(2) and ADC(2)-x], restricted active space second-order perturbation theory, and time-dependent density functional theory—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 isotopic 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 the literature.

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I. INTRODUCTION

Soft X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) are powerful techniques in studies of the molecular electronic structure as they provide 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. 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, CH₃OH, is an important compound used in several practical applications such as renewable fuels and hydrogen storage mediums. In addition, CH₃OH is of principal interest because, in its liquid form, it is a system that like water is dominated by hydrogen-bond interactions—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 have been thoroughly explored using many different experimental techniques including neutron diffraction, X-ray diffraction, X-ray emission spectroscopy (XES), XAS, and RIXS. In the theoretical part of our study, we focus on methanol in the gas phase and on providing an accurate assignment of the associated XAS and RIXS spectra at the oxygen K-edge, as available from the literature. 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 that are obtained in the present work. The O1s X-ray absorption spectra of gas phase methanol were investigated by different groups. Usually, the assignment of the O1s pre-edge XAS spectrum is made by means of calculations based on semiempirical methods, but an exception is found in Ref. 14 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. Another shortcoming of most previous studies is the neglect of nuclear quantum dynamics although it was demonstrated through the RIXS measurements in gas phase methanol and in the liquid phase 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 is similar to the one used in our earlier studies of the RIXS spectrum of water 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. In Sec. IV B, we start the study of RIXS by considering the quasi-elastic channel. In Sec. IV C, we discuss the pseudo-atomic band and the role of isotopic substitution on the RIXS profile. In Sec. IV D, 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 E, we discuss the RIXS process in liquid methanol. 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 \( v_g = (v_0^{(0)}, v_1^{(1)}, v_2^{(2)}, \ldots) \), and ending up in the multimode vibrational state \( v_f = (v_0^{(f)}, v_1^{(f)}, v_2^{(f)}, \ldots) \) of the final electronic state. We adopt the time-dependent representation for the XAS \( \sigma_{\text{abs}}(\omega) \) and RIXS \( \sigma(\omega', \omega) \) cross sections,

\[
\sigma_{\text{abs}}(\omega) = \text{Re} \sum_{\sigma} \langle \Psi(0) | \Psi(\sigma) \rangle,
\]

\[
\sigma(\omega', \omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} e^{i(\omega'-\omega)\tau+i\Pi(t)} \sigma(t) dt,
\]

\( |\Psi(0)\rangle = \sum_{v_r} \frac{D_{v_r}}{\omega - \omega_0 + i\Gamma} |v_r\rangle |D_{v_r}| v_0\rangle \]

where the wave packet \( \Psi(0) \) is given by the same equation as \( |\Psi(\sigma)\rangle \) except that both \( D_v \) and \( D_{\sigma} \) should be replaced by \( \omega_0 \). The RIXS process with the scattering amplitude \( F_{v_r} = \langle v_f | \Psi(0) \rangle \) is affected by nuclear dynamics in the core-excited state and in the final (ground) state as represented in the nuclear wave packets

\[
|\Psi(\sigma)\rangle = e^{-i\hbar \mathcal{C}} (D_{\sigma}|\psi_\sigma\rangle), \quad |\Psi(t)\rangle = e^{-i\hbar \mathcal{T}} |\Psi(0)\rangle.
\]

Here, \( \omega_0, \mathcal{C} \) and \( \mathcal{T} \) are the frequencies and polarization vectors of incoming and scattered photons, respectively, \( \omega_0 \) is the spacing between minima of the potential energy surfaces of the electronic states \( i \) and \( j \), with \( i, j = 0, c, f \) denoting the ground 0, core-excited c, and final f electronic states, respectively; \( \Gamma \) and \( \Gamma_f \) are the lifetime broadenings of the core-excited and final states, respectively. Note that throughout the text, \( \mathcal{C} \) refers to the half-width at half-maximum (HWHM) value. The transition amplitudes \( D_{\sigma}(\mathcal{C}D_{\sigma}) \) and \( D_{\sigma}(\mathcal{C}D_{\sigma}) \) 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 excited above the dissocia-
tion limit. They require special treatment due to the continuity of
the vibrational spectrum. The best numerical method for contin-
um states is the time-dependent wave packet technique. Since
degrees of freedom which have bound potentials can be treated more
efficiently in the frequency domain, we will use a mixed represen-
tation 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,

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

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) represen-
tation as the product of wave packet $\psi_i^{(m)}(t)$ and eigenfunction
$|\nu_i = |\nu_i^{(1)}, \nu_i^{(2)}, ..., \nu_i^{(a)}\rangle$,

$$|\psi_i(t)\rangle = e^{-i\epsilon_i t}|\nu_i\rangle, \quad \frac{\partial}{\partial t}|\psi_i\rangle = h_i^{(m)}|\psi_i\rangle,$$

$$h_i^{(n)}|\nu_i\rangle = \epsilon_i|\nu_i\rangle.$$  

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 $|\nu_i\rangle$. Consequently, the initial vibrational state in general
Eq. (2) should be replaced as follows:

$$|\psi_i(t)\rangle = \hat{\mu}_0|\psi_0\rangle, \quad \epsilon_{\nu_i} \to \epsilon_{\nu_0} + \epsilon_{\nu_i}.$$  

Here $(|\mu_0\rangle, \epsilon_{\nu_0})$ and $(|\nu_0\rangle, \epsilon_{\nu_0})$ are the eigenfunctions and eigenval-
ues of the ground state Hamiltonians $h_0^{(m)}$ and $h_0^{(n)}$, respectively. Using a condition of completeness, 1 = $\sum|\nu_i\rangle\langle\nu_i|$, and $\exp(-i\epsilon_0 t) = \exp(-ih_0^{(m)} t) \exp(-ih_0^{(n)} t)$, one can get the following expression for the wave packet in Eq. (2):

$$|\psi_c(t)\rangle = e^{-i\epsilon_0 t}|\nu_0\rangle e^{-i\epsilon_1 t}|\nu_1\rangle e^{-i\epsilon_2 t}|\nu_2\rangle = \sum \epsilon_{\nu_i} e^{-i\epsilon_i t}|\nu_i\rangle \langle\psi_i^{(m)}(t)|,$$

$$|\psi_i^{(m)}(t)\rangle = e^{-i\epsilon_i t}D_{\nu_i}\hat{\mu}_0.$$  

Now, we are at liberty to rewrite the expression for the wave packet
$|\psi(0)\rangle$ in Eq. (1),

$$|\psi(0)\rangle = \sum |\nu_i\rangle \langle\psi_i^{(m)}(0)|,$$

$$|\psi_i^{(m)}(0)\rangle = D_{\nu_i} \int_0^{\infty} e^{i(\epsilon_0 t - \epsilon_1 t - \epsilon_2 t)} |\psi_i^{(m)}(t)| dt,$$

and for the wave packet $|\psi(t)\rangle$, we get

$$|\psi(t)\rangle = e^{-i\epsilon_0 t}|\nu_0\rangle \sum |\nu_i\rangle \langle\psi_i(t)|,$$

$$|\psi_i(t)| = e^{-i\epsilon_i t}\sum |\nu_j\rangle \langle\psi_j\rangle \langle\psi_i(t)|,$$

$$|\psi_i(t)\rangle = e^{-i\epsilon_i t}|\nu_i\rangle.$$  

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

$$\sigma_{\theta\theta}(\omega) = \frac{Re}{|\mu_0| |\psi_i(0)|^2} \sum |\nu_j\rangle \langle\psi_j|,$$

$$\sigma(\omega, \omega') = \frac{1}{|\mu_0| |\psi_i(0)|^2} \sum \langle\nu_j|\nu_j\rangle \langle\psi_j|\psi_j\rangle \langle\psi_i(0)|^2,$$

$$\sigma_{\gamma\gamma'}(t) = (\psi_i^*\Psi_{\gamma\gamma'}(0)|\Psi_{\gamma\gamma'}(t)),$$

where $|\Psi_{\gamma\gamma'}(0)\rangle$ is defined similarly as $|\psi(0)\rangle$ [see Eq. (1)].

C. Polarization dependence

In the current study, we will ignore the change in the transition
dipole moment during the course of nuclear motion and we use the equilibrium values for $d_{\nu\nu}$. Since we explore the XAS and
RIXS spectra of gas phase methanol, the cross sections should be averaged over isotropic molecular orientations using equations

$$(\mathbf{e} \cdot \mathbf{d}_{\nu\nu})^2 = \frac{d_{\nu\nu}^2}{3}$$

and

$$(\mathbf{e} \cdot \mathbf{d}_{\nu\nu})(\mathbf{e} \cdot \mathbf{d}_{\nu\nu})(\mathbf{e} \cdot \mathbf{d}_{\nu\nu}) = \frac{d_{\nu\nu}^2 d_{\nu\nu}^2}{30} (3 + \cos^2 \chi + (1 - 3 \cos^2 \chi) (\mathbf{d}_{\nu\nu} \cdot \mathbf{d}_{\nu\nu}))^2.$$  

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

$$(\mathbf{d}_{\nu\nu} \cdot \mathbf{d}_{\nu\nu}) \propto d_{\nu\nu}^2 d_{\nu\nu}^2 (3 + \cos^2 \chi),$$

$$(\mathbf{d}_{\nu\nu} \cdot \mathbf{d}_{\nu\nu}) \propto d_{\nu\nu}^2 d_{\nu\nu}^2 [3 + \cos^2 \chi + (1 - 3 \cos^2 \chi) (\mathbf{d}_{\nu\nu} \cdot \mathbf{d}_{\nu\nu})^2].$$

Bear in mind that the transition dipole moments $\mathbf{d}_{\nu\nu}$ and $\mathbf{d}_{\nu\nu}$ are not necessarily parallel to each other despite that both lie in the symmetry plane of the equilibrium geometry.
D. Electronic structure theory calculations

The ground-state electronic configuration of methanol is \((1\alpha')^2, (2\alpha')^2, (3\alpha')^2, (4\alpha')^2, (1\alpha'')^2, (5\alpha')^2, (6\alpha')^2, (7\alpha')^2\), and \((2\alpha'')^2\), where the \(1\alpha'\)-orbital is the atomic oxygen \(1s\)-orbital. To shed light on the electronic structure of the methanol molecule in the ground state and the O1s core-excited states, it is useful to consider the natural orbitals. Figure 1 shows the occupied natural orbitals of the electronic ground state and the low-lying oxygen core-excitation) refer in these cases to canonical Hartree–Fock or Kohn–Sham excitation vectors (the eigenvectors of the respective secular equation). 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 multireference 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.34,35 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.36,37 With this approach, 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 functional31,32 display an agreement with the experiment results reported in Ref. 33 that agrees with the experiment results reported in Ref. 33 that agrees with the experiment results reported in Ref. 33 that agrees with the experiment results reported in Ref. 33 that agrees with the experiment results reported in Ref. 33 that agrees with the experiment results reported in Ref. 33.
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. 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 algebraic diagrammatic construction (ADC) polarization propagator method, which has been shown to provide an excellent description of coreexcitation processes\(^{21}\) 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 for.\(^{22}\)

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,\(^{23,24}\) which has recently been combined with ADC.\(^{25}\) 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 relations.\(^{26}\) 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 the CVS approximation), and this has in turn enabled the derivation and implementation of the full electronic polarization propagator for inelastic scattering such as RIXS.\(^{27}\) 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.\(^{28,29}\)

### III. COMPUTATIONAL DETAILS

The geometry optimization and Hessian calculation were performed in C\(_3\) symmetry on the level of DFT/B3LYP\(^{31,32}\) functional and aug-cc-pVTZ basis set\(^{33}\) in the Gaussian09 software,\(^{34}\) 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\(^{35,36}\) with the ANO-RCC-VTZP\(^{37}\) basis set (see Table I) and using the MOLCAS program (version 8.2)\(^{38}\) without imposing symmetry and with 12 electrons in an active space of 12 orbitals. For the calculation of core- and valence-excited states and corresponding transition dipole moments, we used three different methods [restricted active space second-order perturbation theory (RASPT2), CPP-ADC(2), and TDDFT], which are described in detail below.

The computation of ground and core-excited states was performed with the RASSCF method\(^{39}\) followed by RASPT2.\(^{40}\) These calculations were scalar relativistic, as implemented in the MOLCAS code (version 8.2)\(^{41}\) using the Douglas-Kroll-Hess formulation\(^{42,43}\) and the ANO-RCC-VTZP\(^{37}\) basis set. The transition dipole moments between the studied electronic states were calculated within the RASSI approach.\(^{44}\) The core excitation energies and transition dipole moments presented as RASPT2 in Table II were computed at the equilibrium geometry, using an extended Rydberg basis set (8s8p6d) and the C\(_3\) symmetry. Proper treatment of the transition dipole moments is ensured by using the “highly excited-state” (HEXS) approach\(^{45}\) within the RASSCF method. The three orbitals having atomic orbital characters C1s (2\(\alpha'\)) and combinations of O2s + C2s (3\(\alpha'\)) and O2s-C2s (4\(\alpha'\)) were kept inactive. The O1s (1\(\alpha'\)) 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-excitation states and to one for core-excited states. The full active space consisted of 13 orbitals, namely, the O1s orbital, five of the occupied orbitals having valence character: 1\(\alpha''\), 5\(\alpha'\), 6\(\alpha'\), 7\(\alpha'\), 2\(\alpha''\), and the seven lowest unoccupied orbitals: 8\(\alpha'\), 9\(\alpha'\), 3\(\alpha''\), 10\(\alpha'\), 11\(\alpha''\), 12\(\alpha'\) and 4\(\alpha''\). The ground state was obtained by a state-specific

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**TABLE I. Experimental\(^{1}\) and theoretical (DFT) frequencies of vibrational modes of methanol in the ground state.**

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Sym.</th>
<th>Expt. cm(^{-1})</th>
<th>Theor. (DFT), cm(^{-1})</th>
<th>Theor. (CASPT2), cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torsion</td>
<td>(v_{12})</td>
<td>(\alpha')</td>
<td>295 (0.036)</td>
<td>296 (0.037)</td>
</tr>
<tr>
<td>CO stretching</td>
<td>(v_8)</td>
<td>(\alpha')</td>
<td>1033 (0.128)</td>
<td>1039 (0.129)</td>
</tr>
<tr>
<td>CH(_3) rock</td>
<td>(v_7)</td>
<td>(\alpha')</td>
<td>1060 (0.131)</td>
<td>1076 (0.133)</td>
</tr>
<tr>
<td>CH(_3) rock</td>
<td>(v_{11})</td>
<td>(\alpha'')</td>
<td>1165 (0.144)</td>
<td>1170 (0.145)</td>
</tr>
<tr>
<td>OH bending</td>
<td>(v_6)</td>
<td>(\alpha')</td>
<td>1345 (0.167)</td>
<td>1365 (0.169)</td>
</tr>
<tr>
<td>CH(_3) s-deform.</td>
<td>(v_5)</td>
<td>(\alpha')</td>
<td>1455 (0.180)</td>
<td>1477 (0.183)</td>
</tr>
<tr>
<td>CH bending</td>
<td>(v_{10})</td>
<td>(\alpha'')</td>
<td>1465 (0.182)</td>
<td>1498 (0.186)</td>
</tr>
<tr>
<td>CH bending</td>
<td>(v_4)</td>
<td>(\alpha'')</td>
<td>1477 (0.183)</td>
<td>1508 (0.187)</td>
</tr>
<tr>
<td>CH stretching</td>
<td>(v_3)</td>
<td>(\alpha')</td>
<td>2844 (0.353)</td>
<td>2994 (0.371)</td>
</tr>
<tr>
<td>CH stretching</td>
<td>(v_9)</td>
<td>(\alpha'')</td>
<td>2960 (0.367)</td>
<td>3040 (0.377)</td>
</tr>
<tr>
<td>CH(_3) d-stretching</td>
<td>(v_2)</td>
<td>(\alpha')</td>
<td>3000 (0.372)</td>
<td>3109 (0.385)</td>
</tr>
<tr>
<td>OH stretching</td>
<td>(v_1)</td>
<td>(\alpha')</td>
<td>3681 (0.456)</td>
<td>3829 (0.475)</td>
</tr>
</tbody>
</table>
TABLE II. Vertical transition energies (eV) (oscillator strengths, f × 10^2) of O(1 s⁻¹) core-excitation from RASPT2, ADC(2)-x, and REW-TDDFT simulations (see Sec. III for details).

<table>
<thead>
<tr>
<th></th>
<th>8Ω''</th>
<th>9Ω''</th>
<th>3Ω''</th>
<th>10Ω''</th>
<th>11Ω''</th>
<th>12Ω''</th>
</tr>
</thead>
<tbody>
<tr>
<td>RASPT2</td>
<td>535.04 (9.56)</td>
<td>536.59 (2.83)</td>
<td>537.10 (0.82)</td>
<td>537.11 (1.51)</td>
<td>537.62 (2.36)</td>
<td>537.85 (4.46)</td>
</tr>
<tr>
<td>ADC(2)-x</td>
<td>533.05 (8.97)</td>
<td>534.82 (3.23)</td>
<td>535.14 (2.31)</td>
<td>535.15 (1.26)</td>
<td>535.68 (3.35)</td>
<td>535.97 (5.07)</td>
</tr>
<tr>
<td>REW-TDDFT</td>
<td>519.34 (7.61)</td>
<td>521.17 (2.86)</td>
<td>521.47 (4.23)</td>
<td>521.56 (1.94)</td>
<td>522.16 (7.82)</td>
<td>522.48 (6.22)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>4Ω''</th>
<th>13Ω''</th>
<th>14Ω''</th>
<th>5Ω''</th>
<th>6Ω''</th>
</tr>
</thead>
<tbody>
<tr>
<td>RASPT2</td>
<td>538.02 (0.11)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>ADC(2)-x</td>
<td>536.13 (0.001)</td>
<td>536.15 (4.71)</td>
<td>536.23 (1.42)</td>
<td>536.25 (0.23)</td>
<td>536.35 (1.91)</td>
</tr>
<tr>
<td>REW-TDDFT</td>
<td>523.08 (3.92)</td>
<td>523.23 (3.81)</td>
<td>523.45 (2.69)</td>
<td>523.46 (0.90)</td>
<td>523.60 (11.63)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>7Ω''</th>
<th>8Ω''</th>
<th>9Ω''</th>
<th>10Ω''</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC(2)-x</td>
<td>537.31 (0.89)</td>
<td>537.37 (0.69)</td>
<td>537.45 (0.11)</td>
<td>537.62 (0.1)</td>
</tr>
<tr>
<td>REW-TDDFT</td>
<td>524.38 (1.83)</td>
<td>524.39 (5.13)</td>
<td>525.29 (0.56)</td>
<td>526.24 (0.41)</td>
</tr>
</tbody>
</table>

The PECs of ground and core-excited states were computed along the distortion vectors of 11 normal modes. Because the torsion mode ν6 (Table I) has too low frequency (0.036 eV) to be resolved in a RIXS experiment, this mode was excluded from our calculations.

The PEC 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). The active space was identical to the one described above except that the 4Ω'' orbital was removed due to convergence problems. 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 C2v point group, whereas for the A''′ symmetry, the C1v 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 program using the restricted energy window (REW) approach, which in essence is the same as the CVS approximation. The range-separated CAMB3LYP functional was used with the parameterization proposed in Ref. 43 for core-excitations and in conjunction with Dunning’s aug-cc-pVQZ basis set.

Based on the core-transitions calculated with above methods, the XAS and RIXS cross sections [Eq. (9)] were calculated with the use of a modified version of the eSspe program. The numerical solution of the equations presented in Sec. II B was carried out as described in Ref. 26. 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(λe+m), N being the number of grid points along each dimension. Instead, we only need to solve k × N^m 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^m 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, and TDDFT) as described in Sec. III. The results of calculations of oscillator strengths f and transition energies are collected in Table II. The corresponding XAS cross sections (Fig. 2), computed with Γ = 0.08 eV and neglecting nuclear motion, display rather strong sensitivity of the XAS profile to the theoretical method. The oscillator 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 resonance:

$$\sigma_{abs}(\omega_{res}) = \frac{e^2}{2m_e c \epsilon_0 \Gamma}.$$  (13)

We will see below that the theory (Fig. 2) cannot 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. 33. To understand the influence of nuclear motion on the XAS, we start with a 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 \( \nu_{12} \) 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 \( \nu_1 \) (OH-stretching) which is dissociative in the \( 8\sigma' \) core-excited state, \( \nu_8 \) (CO-stretching) which is pseudodissociative in the \( 8\sigma' \) and \( 9\sigma' \) core-excited states, and \( \nu_7, \nu_6, \) and \( \nu_5 \) (CH\(_3\)-rock, OH-bending, and CH\(_3\) s-deformation,

![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.](image)
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 subset of four modes (out of the five modes in Fig. 3) are active for each individual core-excited state,

\[
\begin{align*}
8A': & \quad 1D(v_1) + 3D(v_8, v_5, v_6) \\
9A': & \quad 1D(v_8) + 3D(v_7, v_5, v_6) \\
10A': & \quad 1D(v_8) + 3D(v_7, v_5, v_6) \\
11A': & \quad 1D(v_7) + 3D(v_8, v_5, v_6) \\
12A': & \quad 1D(v_7) + 3D(v_8, v_5, v_6).
\end{align*}
\]

Here, we order the vibrational modes according to the 1\(D + 3D\) model outlined in Sec. II B as a general \(mD + nD\) representation. Hence, for each core-excitation, the mixed representation treats one mode in the time domain and three modes in the frequency domain. This subselection shown in Eq. (14) was performed as follows. Mode \(v_1\) 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 \(v_7\) 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 1\(D + 3D\) model using Eq. (9) and \(\Gamma = 0.08\) eV as the lifetime broadening (HWHM) of the O1s core-hole. Here and below, we neglect the dependence of the transition dipole moment on nuclear coordinates, taking \(d_{c0}\) as calculated at the equilibrium geometry. Results of the simulation are depicted in Fig. 4.

A 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 \(v_1\) mode becomes repulsive under core-excitation, similar to gas phase and liquid water, where the molecule dissociates into a hydrogen atom and a core-excited methoxy radical \(\text{CH}_3\text{O}^\ast\). We see that the agreement with experiment 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 experiment from the point of view of both intensity distribution and the peak positions (Fig. 4). Let us note that here we compare the transition dipole moments and

![Figure 4](https://example.com/fig4.png)

**FIG. 4.** XAS spectrum of the gas phase of methanol at the O K edge taking into account nuclear motion compared to experiment. 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.
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 the two lowest core excited states \( 8a'^1 \) (Fig. 5) and \( 9a'^1 \) (Fig. 6). As one can see from the PECs (Fig. 3), methanol dissociates along the OH bond in the first core-excited state, \( 8a'^1 \), while all modes have bound PECs for the second core-excited state, \( 9a'^1 \). This is the main reason for such a strong difference in the vibrational progression of \( 8a'^1 \) and \( 9a'^1 \) 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 \( 8a'^1 \) core-excited state

When the photon energy is tuned in resonance with the \( 8a'^1 \) 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 lifetime in the dissociative PEC of the \( 8a'^1 \) state. This results in the population of high \( \nu_1 \) 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 \(^{27,28}\) 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 \( n = (\nu_1, \nu_5, \nu_6, \nu_8) \) composed of the active modes in this channel [see Eq. (14)].

Due to ultrafast 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 (\( \text{CH}_3O^* \)), results in the appearance of a peak at \( \omega - \omega' = 8 \text{ eV} \), which we denote as the atomic-like peak, following the well-established terminology used for ultrafast dissociation in diatomic molecules. \(^{27,28,61}\) Note that the width of the atomic-like peak is significantly larger than the natural broadening (HWHM) \( \Gamma = 0.08 \text{ eV} \) (Fig. 3). The reason for this is the vibrational structure of the methoxy radical.
It is crucial to mention that the atomic-like peak, described here, lies in the same energy region as electronically inelastic features and hence is not observable as an isolated peak. Nevertheless, a closely related feature, which we refer to as a pseudo-atomic peak,

\[ \text{atomic-like peak} \] is formed in the decay to the lowest valence excited state. However, in sharp contrast to the atomic-like peak, it is formed close to the equilibrium geometry. We will discuss the intricacies of the atomic-like and pseudo-atomic peaks in detail in Sec. IV C.

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

\[ \tau = \frac{1}{\sqrt{|\Omega|^2 + \Gamma^2}}, \]

(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 \( \Omega \) dependence of the RIXS spectra around the 8.5 eV 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 absorption resonance, as shown in Fig. 7. Rayleigh line

\[ \text{librium geometry. Finally, the whole RIXS profile collapses to the} \]

\[ \text{Ω vibrational progression with an increase in} \]

\[ |\Omega| \text{explore the} \]

\[ \text{which is controlled by detuning from the top of the XAS resonance} \]

\[ \Omega = \omega - \omega_{\text{top}}. \]

Immediately to the top of the XAS resonance

\[ \text{at large values of} \]

\[ \Omega \text{due to the decrease in the effective scattering duration} \]

\[ \tau < \text{T}_{\text{vib}} = \frac{2\pi}{\omega_{\text{vib}}}. \]

(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 \( n = (v_8, v_7, v_6, v_5) \) 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 \( 0 \leq \omega - \omega' \leq 1 \text{ eV} \). 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 the 9a′ state is mostly affected by the \( v_8 \) and \( v_5 \) 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 \( v_8 \) and \( v_5 \) modes, respectively, with smaller contributions from the \( v_6 \) and \( v_7 \) modes. The total vibrational progression is made up of \( (v_8, 0, 0, 0) \) and \( (0, 0, 0, v_5) \), and both are dressed by mixed excitations, or overtones. At energy loss \( \omega - \omega' > 0.5 \text{ eV} \), we observe the formation of a “tail” due to the high density of close-lying vibrational levels corresponding to mixed overtones of different modes.

C. Dynamical origin of the splitting of the 2a′′ peak

Let us come back to the RIXS via core-excitation to state 8a′, where methanol dissociates along the normal coordinate \( Q \equiv Q_2 \), which corresponds to elongation of the OH bond. In Sec. IV B 1, the atomic-like feature

\[ \text{at} \omega - \omega' = 8 \text{ eV (Fig. 5)} \]

was discussed and attributed solely to the transition to the ground state of the product of the dissociation, core-excited methoxy radical \( CH_3O^+ \).

\[ \omega + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^+ \rightarrow \text{CH}_3\text{O} \cdot + \text{H} + \omega'. \]

(17)

However, as briefly mentioned at the end of Sec. IV B 1, there is another RIXS channel which also contributes to the features lying in this energy region. This is expected since the methoxy radical belongs to the C_{3v} point group with a doubly degenerate \( X^1 \Sigma^+ \) ground state. Hence, two electronic states of methanol should have the same dissociation limit along the OH stretch, namely, the ground state \( |GS\rangle = |1A'\rangle \) and the dissociative \( |2a''\rightarrow 8a'\rangle \) state (see Fig. 8). Therefore, we need to account for two overlapping RIXS features: The first one studied in Sec. IV B ends up in the ground state \( |GS\rangle \), while the final dissociative valence excited state \( |2a''\rightarrow 8a'\rangle \) gives rise to the second RIXS channel. Let us now investigate the gross features of these channels, namely, the molecular band and the atomic-like peak. For this purpose, we employ a 1D model,

![FIG. 7. Dependence of the RIXS profile on the detuning Ω near the first core-excited state (1a′→8a′)).](attachment:fig7.png)
taking into account only the ν1 mode, which is the most active coordinate.

The computed total RIXS spectra and the partial contributions from each channel are shown in the upper and lower panels of Fig. 9, respectively, for both CH3OH and CH3OD. The quantitative details of the observed dependences on the photon polarization and isotopic substitution will be discussed below; for now, we shall focus on understanding the contributions of different channels to the total
profile. Evidently, both RIXS channels contribute to the atomic-like peak formed in the dissociation region since the ground and valence-excited states have the same dissociative limit (Fig. 8). However, the contribution of the valence channel to this spectral region also involves decay transitions near the equilibrium geometry since the potentials of the core- and valence-excited states become parallel already around $Q \approx 1.0$ a.u. Thereby, a pseudo-atomic peak (marked as $\text{at}''$ in Fig. 9) is formed. The pseudo-atomic peak has the same transition energy but much higher intensity than a real atomic-like peak (marked as $\text{at}''$ in Fig. 9). The reason for this is that only a small fraction of the nuclear wave packet reaches the dissociation region ($Q \geq 3.0$ a.u.) in the core-excited state due to the short lifetime on the core-excited states (Fig. 8). Let us discuss this non-trivial formation of RIXS to the valence excited state in more detail.

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 $\Delta U_{\text{f}}(Q) = U_{\text{f}}(Q) - U_{\text{i}}(Q)$ for final states $|f\rangle = |\text{GS}\rangle$ and $|f\rangle = |2a''^r8a'\rangle$ (Fig. 8). It is well known that the molecular band and the atomic peak, in diatomics, strictly coincide with each other when the PECs of core-excited and final states are exactly parallel. One can see (Fig. 8) that the PEC of the final $|2a''^r8a'\rangle$ state is almost parallel to the one of the core-excited states, contrary to the ground final state. Figure 8 shows that the region of formation of the pseudo-atomic peak, defined by the condition $\Delta U_{\text{f}}(Q) = const$, starts at $Q \approx 1$ a.u. for the valence final state $|2a''^r8a'\rangle$, while for the ground final state, the formation of the atomic-like peak starts for longer distances $Q \geq 3$ 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 the RIXS channel to the ground state, the maxima of the atomic-like peak and the molecular band are separated by $\omega_{\text{mol}} - \omega_{\text{at}} \approx \Delta U_{\text{f}}(0) - U_{\text{f}}(1 \text{ a.u.}) = 0.95$ eV (Fig. 8). By contrast, the scattering to the dissociative $|2a''^r8a'\rangle$ state is expected to have close lying pseudo-atomic and molecular peaks with the spacing of only $\omega_{\text{mol}} - \omega_{\text{at}} \approx \Delta U_{\text{f}}(0) - U_{\text{f}}(1 \text{ a.u.}) = 0.95$ eV (Fig. 8). This expectation is nicely confirmed by the simulated RIXS profile (Fig. 10) with $\omega_{\text{mol}} - \omega_{\text{at}} = 0.76$ eV. We notice that a similar behavior has been observed in the water molecule.  

In summary, despite the fact that they occur at nearly the same emission energy, the nature of the pseudo-atomic and atomic-like peaks arising in the RIXS to the valence-excited and ground states, respectively, is different. The decay in the core-excited fragment of dissociation, the methoxy radical, forms an atomic-like peak when the final state is the ground electronic state. Contrary to the ground state RIXS channel, the origin of the pseudo-atomic peak for the $|2a''^r8a'\rangle$ RIXS channel is mainly the decay transition in CH$_3$OH not far from the equilibrium geometry and its energy position is rather close to the molecular band (Figs. 8 and 10). Despite their inherent differences, they are both dynamical features that behave analogously with respect to isotopic substitution and excitation energy detuning, as we describe below.

Results of the 1D simulations of the RIXS profile, shown in Fig. 10, demonstrate the role of isotopic substitution. First of all, one can see the effect of the isotopic substitution on the vibrational progression, originated from decay to the ground-state. The observed difference is simply caused by the difference in OH and OD vibrational frequencies. The second effect we observe is mainly due to the pseudo-atomic peak, formed upon decay to the $2a''$ state, and is related to the slowdown of the nuclear wave packet in the dissociative core-excited state of CH$_3$OD in comparison with CH$_3$OH, because of the heavier deuterium atom. This makes the pseudo-atomic peak in RIXS of CH$_3$OD less intense than in the CH$_3$OH, which is in good agreement with the experiment (Fig. 10).

There is also another tool to distinguish pseudo-atomic and molecular peaks: The dispersion law. As it is well known, the emission energy of the pseudo-atomic peak should not depend on the excitation energy $\omega$, as opposed to the molecular band which has Raman dispersion (see Fig. 11). 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 $0 \leq \omega - \omega' \leq 5$ eV (see lower panel in Fig. 9). Similarly to the quasi-elastic channel, shown in Fig. 7, the intensity of the pseudo-atomic peak formed in the inelastic channel (Fig. 11) drops as we tune away from the top of the $8\omega''$ XAS resonance. To conclude, one should stress that the RIXS channel to the $|2a''^r8a'\rangle$ final state would have only a molecular peak if the nuclear motion were neglected. However, the dissociation of the core excited methanol molecule along the $\nu_1$ PEC of this state results in an additional resonance, the pseudo-atomic peak. Thus, the splitting of the $|2a''^r8a'\rangle$ resonance is dynamical in nature.

Finally, let us turn our attention to the polarization dependence of the studied RIXS profile which can be significant due to different orientations of the decay transition dipole moments $d_{\text{a},0}$ and $d_{\text{a},\omega'}$ to the ground and to the $|2a''^r8a'\rangle$ states, respectively. Indeed, the transition dipole moments $d_{\text{a},0}$ and $d_{\text{a},\omega'}$ of these channels are orthogonal to each other (see Table III) since the molecular orbital $8a''$ is lying in the molecular plane, while the $2a''$ orbital is orthogonal to this plane because of its $\pi$ character (Fig. 1). Due to this and Eqs. (10)
and (11), the total RIXS cross section in Eq. (9) in the region \( \omega - \omega' \) \( \leq \) 8 eV is the sum of two contributions with different polarization dependences,

\[
\sigma'(\omega', \omega) = \frac{d^2}{30} [2 - 2\cos^2 \chi] \sigma_0 + \frac{d^2}{2} [3 + \cos^2 \chi] \sigma_2 \sigma'.
\] (18)

The partial cross sections \( \sigma_0 \) and \( \sigma_2 \sigma' \) corresponding to the RIXS to the ground and \( |2a''^{9/8}a''^{1/4} \rangle \) states, respectively are computed using Eq. (9) with \( D_{00} = D_{kk} = 1 \) within one-dimensional model (Fig. 8) taking into account only elongation of the OH bond. As expected, the RIXS profile in Eq. (18), shown in Fig. 9, displays a strong scattering anisotropy for both CH$_3$OH and CH$_3$OD.

### D. 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 was 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 \( a' \rightarrow 8a' \) and \( a' \rightarrow 9a' \), 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 Benkert, 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 result 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 than 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 multireference 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.

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

| Transition | \( \mathbf{d}_x \) | \( \mathbf{d}_y \) | \( \mathbf{d}_z \) | \( \mathbf{d} = |\mathbf{d}| \) |
|------------|----------------|----------------|----------------|----------------|
| GS \( \rightarrow |1\sigma_g^{1/2}a''^{9/2} \rangle \) | -0.008 17 | -0.030 40 | 0.000 00 | \( d_{\sigma} = 0.031 48 \) |
| \( |1\sigma_g^{1/2}a''^{9/2} \rangle \rightarrow |2a''^{9/8}a''^{1/4} \rangle \) | 0.000 00 | 0.000 00 | -0.055 19 | \( d_{2\sigma'} = 0.055 19 \) |
This labeling 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 to 0-th order, can be viewed as single-reference states. For 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 8a'' 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 values derived 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 8a'' 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 9a''; in this case, it appears as a shoulder, which is 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 multireference nature of the involved states. As a result, the valence 1A'' state is coupled to the second core-excited state and shows a nonzero transition 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 of 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 9a'' state originates, for example, from weak nonresonant population of the 8a'' 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. Likewise, for the 2A'' state, it appears as a strong peak in the spectrum at the frequency in resonance with the 9a'' state but only as a weak spectral feature at the frequency in resonance with the 8a'' 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 expression.

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'' → 9a'' and 5a'' → 9a'' transitions. Here, the additional peaks besides those originating from the 1a'' and the 6a'' orbitals are a result of transitions 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'' → 1s0 deserves a special comment. Contrary to transitions from other 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'' → 8a'' and 2a'' → 9a'' is very small, 0.088 eV (see Fig. 12). The reason for this is the nonbonding character of the 2a'' orbital which behaves rather similarly to the 1sO orbital (like the 1b1 orbital in H2O molecule). This makes the 2a'' → 1s0 transition very special in RIXS of liquid methanol (see Sec. IV E) and similar to the 1b1 → 1s0 transition in liquid water.

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 $(\mathbf{d}_{a''} \cdot \mathbf{d}_{A''})^2 = 1$,

$$\sigma_{a''A''} \propto 3 + \cos^2 \chi, \quad \sigma_{a''A''} \propto 2 - \cos^2 \chi.$$  \hspace{1cm} (19)

Here, the first channel $\sigma_{a''A''}$ 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 $\sigma_{a''A''}$ in Fig. 12. In agreement with Eq. (19), the
RIXS peaks $2a'' \rightarrow na'$ and $7a' \rightarrow na'$ display opposite dependence on the angle $\chi = \angle (\mathbf{e}, \mathbf{k}')$.

E. 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 the liquid phase. The quasi-elastic RIXS differs qualitatively from electronically inelastic resonant X-ray scattering. This type of RIXS shows a nicely resolved vibrational structure in different aggregate states of matter: crystalline and amorphous solids, liquid acetone, and water. RIXS experiments have been performed at the ADRESS—X03MA beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland, using the SAXES spectrometer 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$_3$N$_4$ 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 O$_2$s spectrum. These new measurements with much better resolution in comparison with the earlier experiment 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 artifacts due to X-ray optics at approximately ±0.65 eV with respect to the elastic line. This artifact, 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 artifact-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 the liquid phase. The experimental quasi-elastic RIXS of liquid methanol displays the OH vibrational progression with a vibrational frequency of $\omega_{v1} = 0.425$ eV which is rather close to the experimental IR frequency $\omega_{v1} = 0.456$ eV (see Table I). One can see that the vibrational progression in the liquid phase is significantly shorter than in gas phase methanol. The reason for this is the strong fluctuation of the 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 water 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 the liquid phase (Fig. 13) due to the broadening of the vibrational resonances by much weaker fluctuation of the OH potential in the inner region.

Let us turn our attention to the split $2a''$ RIXS peak discussed in Sec. IV C. A similar splitting, observed in the RIXS spectra of liquid methanol, has been debated. There are two distinct interpretations of the origin of this splitting—a dynamical and a structural interpretation. Both interpretations use a model based on double-well potentials for core-excitated and final states 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 C for the gas phase. As one can see from Fig. 9, the main contribution to

![Figure 13](image-url)
the region around the $2a''$ RIXS band comes from the RIXS to the dissociative valence $|2a''r'1s'\rangle$ excited state. As already explained in Sec. IV C (see also Fig. 8), the formation of the split $2a''$ peak comes from the decay transitions in core-excited CH$_3$OH in the range rather close to the equilibrium $Q - Q_0 \leq 1$ a.u., where the role of the hydrogen bond network is expected to be weak, similar to liquid water.\(^1\) Here, it is important to remember that the nonbonding $2a''$ orbital is rather similar to the nonbonding $1s_O$ orbital (see also Sec. IV D). Akin to the $1b_1 \to 1s_O$ transition in liquid water, the parallelism of the potentials of the $|2a''r'1s'\rangle$ and $|1s_O^{-1}8a''\rangle$ states is preserved even for longer distances, $Q - Q_0 \geq 1$ a.u.\(^2\) 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 energy.\(^2\)

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 H$_2$O,\(^4\) 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.\(^2,7,8\)

**V. CONCLUSIONS**

We have presented \textit{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,\(^-\) results in a long vibrational progression in the case of RIXS to the ground state. The ground and dissociative $|2a''r'1s'\rangle$ 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 $|2a''r'1s'\rangle$ 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 split $2a''$ 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 \textit{ab initio} simulations quantitatively describe the available XAS\(^16-\)\(^18\) and RIXS\(^5\) 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.

**ACKNOWLEDGMENTS**

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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 spectra 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 the experimental one, the relative energy difference is improved, e.g., the energy difference between 1\(A''\) and 3\(A'\) states is 2.05 eV at the ADC(2)/aug-cc-pVTZ level, while ADC(3)/d-aug-cc-pVTZ provides a value of 1.90 eV, which is closer to the experimental result.

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

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<th>(2A') (2a'' \rightarrow 3a'')</th>
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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 significantly shifted with respect to the ground state PECs (green lines).
TABLE V. Core-valence excitation energies $\Delta E$ (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), and t-aug-cc-pVTZ (tTZ).\(^{48}\)

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