Published in final edited form as:

J Chem Phys. 2016 February 21; 144(7): 074701. doi:10.1063/1.4941377.

Absolute vibrational cross sections for 1–19 eV electron scattering from condensed tetrahydrofuran (THF)

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Abstract

Absolute cross sections (CSs) for vibrational excitation by 1–19 eV electrons impacting on condensed tetrahydrofuran (THF) were measured with a high-resolution electron energy loss spectrometer. Experiments were performed under ultra-high vacuum (3×10^{-11} Torr) at a temperature of about 20 K. The magnitudes of the vibrational CSs lie within the 10^{-17} cm² range. Features observed near 4.5, 9.5, and 12.5 eV in the incident energy dependence of the CSs were compared to the results of theoretical calculations and other experiments on gas and solid-phase THF. These three resonances are attributed to the formation of shape or core-excited shape resonances. Another maximum observed around 2.5 eV is not found in the calculations but has been observed in gas-phase studies; it is attributed to the formation of a shape resonance.

I. INTRODUCTION

Radiotherapy is a major modality for cancer treatment.^{1,2} For each radiotherapy treatment, a medical physicist must calculate the precise dose, spatial distribution, the energy deposited density, and many other parameters before administering radiation to the patient. Such calculations depend on multiple parameters describing the interaction of ionizing radiation with biological matter at the subcellular level.³ The energy deposited by ionizing radiation is transferred into biological matter principally by the secondary electrons it produces.^{3–6} Indeed, a very large quantity of secondary electrons are produced ($\sim 5 \times 10^4$ MeV⁻¹)⁷ and 88% of these will have energy less than 20 eV.⁸ These low energy electrons (LEEs) interact and transfer their energy with the biological medium by multiple inelastic processes, initiating damage to vital biomolecules such as DNA. Secondary LEE can ionize molecules, produce vibrational, rotational, and electronic excitations. The latter can lead to molecular dissociation producing neutral radicals or ions. When the electron attaches to the molecule for sufficient time, dissociative electron attachment (DEA) is also possible.⁹ A thorough and quantitative understanding of these processes is crucial for the development of new physically realistic models of radiation damage processes (e.g., Monte Carlo simulations) and improvement of dose calculations for radiotherapy down to the nanoscopic level.¹⁰

LEEs are particularly important for dose calculations in targeted radionuclide therapy (TRT).

¹¹ This modality is based on the release of Auger electrons from radio-labeled molecules engineered to reach preferentially cancer cells to deliver a high radiation dose to malignant tissues. Auger electrons are considered to be short range particles, because their energy

distribution lies mainly at low energy and extends below 20 eV.⁸ Since in TRT, the radioactive atoms that emit Auger electrons bind to the cancer cells, the resultant initial or generated LEE can cause multiple local damages to the DNA, inducing extreme toxicity, while leaving the more distant healthy cells undamaged.¹¹ This relatively new technique depends crucially on the damage induced by primary and secondary LEE and should therefore benefit from a better understanding of the interactions of LEE with biological matter and dose calculations for deposition of their energy. Thus, new spectroscopic data and interaction probabilities (i.e., cross sections) are needed, particularly absolute cross sections (CSs), for LEE interactions with DNA and its various constituents, such as the basic subunits (i.e., the bases, sugar and phosphate groups).

In previous electron impact studies from our group, absolute vibrational and electronic excitation cross sections were measured for the condensed DNA bases pyrimidine, cytosine, and adenine.^{12–15} However, absolute cross sections for other important constituents of DNA remain to be measured, including the deoxyribose molecule which links to phosphate groups in the backbone. Here, we report *absolute* CSs for vibrational excitation by 1–19 eV electrons impacting on condensed tetrahydrofuran (THF). THF (C₄H₈O) serves as a convenient model for the furyl ring at the center of the deoxyribose molecule.^{4,16–24} There exist multiple studies of electron scattering from THF,^{4,16,18,24–28} but *absolute* CSs, necessary for dose calculations, are not available in the condensed phase.

II. EXPERIMENT

Multiple electron energy loss (EEL) spectra were measured with high-resolution electron energy loss spectrometer (HREELS), which has been described in detail previously. Basically, it consists of two hemispherical electrostatic deflectors, i.e., a monochromator and an analyzer.²⁹ These elements are housed within a cryopumped ultra-high vacuum (UHV) chamber that reaches a base pressure of about 3×10^{-11} Torr. In the present experiment, the monochromator, which can be oriented from 14° to 70°, is set at an angle of 15° with respect to the normal of the sample surface. The analyzer is fixed at 45° in the opposite azimuth. The combined energy resolution of the monochromator and the analyzer is about 20 meV full width at half maximum (FWHM). An incident current (I_0) of 0.23 nA is used in all measurements. The determination of I_0 , which is crucial for the calculation of absolute CSs, has been described in detail by Lévesque *et al.*¹² The targets are deposited on a 0.0075 mm thick polycrystalline Platinum (Pt) foil, which is in contact with the head of a closed-cycle cryopump held at about 20 K. The Pt substrate is cleaned by resistive heating to a temperature of 1100 K for about 5 s.

THF, in its vapor state, is introduced into the UHV chamber via a gas-handling manifold, as previously described.²⁹ In the present experiments, a monolayer (ML) of THF (Sigma-Aldrich, 99%) is condensed onto a 3-ML thick layer of Ar (Matheson of Canada Ltd., 99.9995%) previously condensed on the Pt substrate. The amount of vapor or gas introduced in the UHV chamber is measured by the differential pressure drop (ΔP) in the expansion chamber of the gas-handling manifold.²⁹ In this experiment, the differential pressure drop for condensing one monolayer of THF on the Pt substrate is about 1.4 mTorr. This differential pressure drop is then converted to an absolute surface number density (n_s) with

the relation $n_s = (2.04 \times 10^{14} \text{ cm}^{-2} \text{ mTorr}^{-1}) P$. A value of $2.86 \times 10^{14} \text{ cm}^{-2}$ is obtained for the THF monolayer. The conversion factor is established from the P needed to grow a (111) mono-layer of Ar on the Pt substrate at 20 K.^{30,31} The combined uncertainty from the P ($\pm 2.5\%$) and the conversion factor ($\pm 7.5\%$) is about $\pm 10\%$.³²

The THF sample is used without further purification after degassing by repeated freeze-thaw cycles under vacuum. The three-monolayers spacer of Ar serves to prevent the molecular decomposition of THF on the Pt substrate³³ and avoids the proximity effects of the Pt surface. Argon is used because it forms an inert substrate and the electron scattering is mainly elastic due to the large electronic band gap in this rare-gas solid.^{12,34,35}

III. SCATTERING MODEL AND MEASUREMENT PROCEDURE

We previously presented a multiple scattering theory to describe electron scattering from a disordered molecular multilayer film deposited on an inert substrate.³⁶ However, since the thickness of the single layer of THF deposited in the present experiments is much smaller than the electron mean free path, only single collisions within the film were considered.³⁴ In this case, for an incident electron beam current I_0 of energy E_0 , where the scattering symmetry is almost cylindrical (i.e., with θ_0 near normal incidence), it can be shown that the analyzer measures, in the backscattered direction θ_d , a current I of electrons that have transferred an energy of $E - E_0$ into the film such that^{12,34}

$$I(\theta_d, E_0, E - E_0) \cong \frac{I_0(\theta_d, E_0)}{\cos \theta_0} \sigma_r(E_0, E - E_0) n_s. \quad (1)$$

In Eq. (1), $I_0(\theta_d, E_0)$ is defined as an effective incident electron current. The latter can be seen as that fraction of the incident electron current I_0 that would be backscattered into the analyzer positioned at θ_d along the same direction as the detected inelastic current $I(\theta_d, E_0, E - E_0)$ by a material with a diffuse elastic reflectivity of one, assuming that all incident electrons are scattered out of the film.¹²

In the present experiment, for the vibrational CSs, a value of $12\,762 \text{ counts s}^{-1} \text{ eV}$ ($\pm 3\%$) was obtained for $I_0(\theta_d, E_0)$ at $\theta_d = 45^\circ$. This value was obtained by condensing increasing amounts of THF vapor onto the Pt substrate and using the conversion law between the backscattered and transmitted current, as described in detail previously.^{12,34} The quantity $\sigma_r(\theta_d, E_0, E - E_0)$ represents the CS for an electron of energy E_0 to deposit an energy of $E - E_0$ in the film and be backscattered into the vacuum (i.e., differential CS integrated over the whole half-angular space in the backward direction).¹² The value n_s is the surface number density of molecules on the substrate corresponding to the thickness of the film calculated previously. Finally, the factor $1/\cos \theta_0$ accounts for the projection of the incident electron beam section onto the film surface.¹²

To determine the absolute CSs values, multiple EEL spectra $I(\theta_d, E_0, E - E_0)$ are recorded at different E_0 in the direction θ_d on the THF target. Subsequently, each spectrum is fitted with multiple Gaussian functions, each representing a vibrational excitation produced by the

impact of electrons centered at a precise electron energy loss. Given the above $I_0(\theta_d, E_0)$ along with n_s , $\sigma_r(\theta_d, E_0, E - E_0)$, the absolute CS value for each excitation at the precise energy loss is obtained from the area under the corresponding Gaussian function using Eq. (1).

IV. RESULTS AND DISCUSSION

A. Vibrational spectra

Vibrational EEL spectra for 1 ML of THF deposited on the Ar spacer were recorded for electron incident energies E_0 between 1.5 and 18.5 eV. Spectra were measured at every 0.5 eV for incident energies from 1.5 to 6.5 eV, at every 1 eV for energies between 7.5 and 14.5 eV, and at every 2 eV from 14.5 to 18.5 eV. A representative electron energy loss spectrum is shown in Fig. 1. The structures are consistent with the earlier work of Lepage *et al.*,¹⁸ who investigated vibrational and electronic excitation in multilayer THF films under electron impact. The strong peak near zero energy loss corresponds to the detection of electrons backscattered from the target with no energy loss and very small energy losses to phonons (e.g., from the Ar space³⁷) and unresolved vibrational modes of THF. At higher energy loss, up to 400 meV, the deconvoluted peaks correspond to the excitation of various fundamental vibrational modes of the THF molecule. Between 225 and 330 meV and beyond 400 meV the broader features are due to various combinations of multiple vibrational modes. The thin solid line that passes through the experimental data points corresponds to the sum of the multiple Gaussian functions used to fit the vibrational energy loss features. The dashed line represents a background contribution from electrons scattered from the Ar spacer and the Pt substrate.³⁷ The assignments, energies, and the widths (FWHM) of the fundamental vibrational bands observed are listed in Table I along with their excitation energies obtained from optical (Raman and infrared) spectroscopy.³⁸ As shown in Fig. 2 spectra similar to those of Fig. 1 were recorded at the other incident energies E_0 between 1.5 and 18.5 eV. They were also fitted with multiple Gaussian functions. The energies and the FWHM assigned to each vibrational peaks were the same between spectra and only the amplitudes of the Gaussian functions were varied to produce the fits.

In the very low energy-loss region, the peak ν_{33} (17 meV) is produced by the ring puckering and the β -CH₂ twisting. The next mode ν_{17} (37 meV) also arise from ring puckering. The two next modes, ν_{32} and ν_{16} (73 and 81 meV respectively), are ascribed to the β -CH₂ rocking and the ring bending. The broad maximum ν_{15} (102 meV) involves α - and the β -CH₂ rocking of the THF molecule. The next vibrational band, ν_{13} (114 meV), includes the C $_{\beta}$ C $_{\beta}$ stretching and the C $_{\alpha}$ C $_{\beta}$ symmetric stretching. The vibration ν_{28} (131 meV) is due to the C–O–C asymmetric stretching. The next structure containing three maxima ν_{10} , ν_{26} , and ν_8 (146, 156, and 163 meV) is ascribed to the α - and β -CH₂ twisting motions and the β -CH₂ wagging motions of THF. The last vibration modes observed in this structure, ν_6 and ν_5 (181 and 187 meV), are attributed to the bending of α - and β -CH₂ from the THF molecule. The next structure observed in the vibrational spectra constitutes two vibration modes, ν_4 and ν_2 (357 and 371 meV). These vibration bands involve α -CH₂ symmetric and asymmetric stretching of the THF, respectively. Further information about the vibration modes of THF is given in the work of Lepage.¹⁸

B. Vibrational scattering cross sections

The energy dependence of the CSs and their numerical values are presented in Fig. 3 and Table II, respectively. Only vibrations associated with energy losses greater than 105 meV are considered, because contributions from the elastic peak, multiple scattering to phonons, and those of the vibrational modes ν_{33} , ν_{17} , ν_{32} , ν_{16} , and ν_{15} of THF could not be separated. For each incident energy E_0 , the CSs $\sigma_r(E_0, E - E_0)$ were calculated from the area of the corresponding Gaussian energy distribution ($I(\theta, E_0, E - E_0)$), using Eq. (1) along with the experimental parameters: $I_0(\theta, E_0)$, n_s , and $\cos \theta_0$. The $\pm 10\%$ error bars on data points of Fig. 3 indicate the uncertainty related to the Gaussian curve fitting to the experimental spectra of Fig. 2. The error bars neither include uncertainties associated with the stability of the incident current over time ($\pm 5\%$), nor systematic errors in the effective incident current $I_0(\theta, E_0)$ ($\pm 3\%$), or those in the determination of the molecular coverage n_s ($\pm 10\%$). These three latter uncertainties affect only the magnitude of the vertical scale of the Fig. 3. The total absolute error on the present CSs amounts to $\pm 28\%$.

As shown in Fig. 3, the CSs for all studied vibrational modes lie within the 10^{-17} cm^2 range. They share certain similarities: the largest features are observed at incident electron energies below $\sim 6 \text{ eV}$, whereas above 15 eV the magnitude of the CSs is much smaller. This behavior, well-known from gas-phase studies,^{21,39,40} is usually attributed to the formation of short-lived transient anions (i.e., electron resonances) in the low-energy range. In Fig. 3, we can tentatively identify several sections of enhanced excitation, which are indicated in the figure, by the colored rectangles, as region 1 grey (2–3 eV), 2 blue (4–6 eV), 3 green (8–10.5 eV), and 4 yellow (11.5–13.5 eV). Not all structures are present in each region. For example, the vibration mode ν_2 (371 meV) does not show a resonance at high energy, in region 4 between 11.5 and 13.5 eV. The energies of the resonances observed in the colored rectangles for each vibration mode of THF are given in Table III. The CSs for the mode ν_5 (187 meV) seem less precise than those of the other vibrational modes; this is perhaps the result of deconvoluting a vibrational mode located at the “end” of a group of closely lying energy loss features. Indeed, the mode ν_5 was more difficult to fit than its neighbors and hence we observe an increased dispersion in its value with incident electron energy.

As in the case of previous gas- and condensed-phase studies,⁴¹ the structures or enhancements observed at specific energies in the various vibrational CSs can be interpreted as due to the formation of transient anions. Considering the broad widths of the features in the CSs or short lifetimes of the transient anions, the additional electron is considered to attach to the molecule for a time shorter than a vibrational period.^{42,43} Nevertheless, the resonance lifetime is sufficient to allow for relative displacement of the nuclei of the molecule, owing to the bonding or anti-bonding character of the orbital occupied by the captured electron. After autoionization of the anion, the nuclei move back to their original inter-nuclear distances, a process that enhances the vibrational CSs. The short lifetime is usually attributed to the nature and number of decay channels, as well as the form of the electron-molecule potential. When the latter contains a centripetal barrier, the incoming electron is captured at an energy lying above the ground or excited neutral parent states. Particularly above approximately 3 eV, the quasi-bound electron can easily leak through the centripetal barrier, which translates into lifetimes usually smaller than a vibrational period,

producing broad features in vibrational excitation CSs.⁴³ Such transient anion states are referred to as shape or core-excited shape resonances, respectively.⁴⁴ Both types of transitory states can decay into their neutral parent states, which also contributes in reducing their lifetimes.⁴⁴

In this present study, we observe four resonances in the CSs: two with strong magnitude around 2.5 and 4.5 eV and two others at 9.5 and 12.5 eV, which are less intense. It is possible to compare these results with other earlier vibrational intensity measurements or other related studies on the collision of electrons with the THF. Lepage *et al.*¹⁸ reported the intensity of multiple vibration modes of THF as a function of incident electron energy. Several similarities can be seen between the two studies. Lepage *et al.*¹⁸ identified two resonances at 4 and 7.5 eV, which decayed into many vibrational levels. However, the relative intensity of these resonances is different than those observed here at 4.5 and 9.5 eV: the higher-lying feature has a larger intensity in the work of Lepage *et al.*¹⁸ These authors electron bombarded multiple layers (16 ML) of THF, which is expected to lower the energies of transient anions owing to the polarization potential induced by the temporary negative charge in THF. The different energies of the transient anions necessarily affects their decay into different inelastic channels and hence their intensities. In any case, differences are expected between the two studies, since our vibrational peaks were deconvoluted to generate CSs and our spectra are essentially devoid from multiple electron scattering within THF. Interestingly, the resonance we observe at 12.5 eV can be inferred from the work of Lepage *et al.*, by comparing the intensity they recorded for the ν_6 and ν_{10} modes to the vanishing intensity of the ν_2 mode.¹⁸ Similarly in the present investigation, this small maximum is present in all the modes except the mode ν_2 (371 meV). Considering the much different thicknesses of the film in the two experiments, our results are in remarkable agreement with those of Lepage *et al.*

The energies of the resonances in Table III can also be compared to those observed by Allan in the vibrational excitation CSs of gas-phase THF.⁴⁰ In this work, the vibrational intensities exhibit peaks at 6.2 and 10.8 eV for the C–C stretch (ν_{13} (114 meV)), which can be correlated to our results at 4.5 and 9.5 eV. Although the downward shifts are quite different, they possibly can be attributed to induced polarization in the solid state. A 1.7 eV shift for the lower-energy resonance would correspond to a value close to full electronic polarization, whereas the 1.3 eV shift of the higher-energy resonance might indicate that the resonance lifetime is too short to allow for full electronic polarization of the surrounding atoms and molecules (i.e., the shorter lifetime restricts complete orientation of the molecular and atomic orbitals toward the temporary charge, thus reducing the depth of the induced polarization potential). Alternatively, the differential shifts in energy upon condensation for the two anion states may also reflect differences in the spatial extent of their electronic wave functions. States having a larger extent are expected to experience greater repulsive interaction with their local environment which without polarization would result in an increase in excitation energy relative to the gas phase. Thus, if the spatial extent of the 9.5 eV resonance were larger than that of the 4.5 eV state (for example by having a greater Rydberg character) then this secondary process would act against the effects of polarization and result in a smaller net-stabilization. Such effects have been proposed to explain the apparent blue-shift upon condensation of anion states of H₂O.^{45,46} The difference in the

structure intensities between the two results can, at least partially, be attributed to our deconvolution procedure. Moreover, the resonance, which clearly appears at about 2.5 eV in the vibrational CSs (grey rectangle Fig. 3) for excitation of the ν_5 mode, is also observed in many other vibration modes in our work and that of Allan for the ν_6 mode (181 meV) of THF. Similarities can be seen with the resonant structures found in cyclopentane, ethylene oxide, and cyclopropane, where a low-lying resonance can be found around 2.6 eV only in the cross section for the excitation of the CH_2 scissoring vibration (ν_6 (181 meV)).^{40,47} This feature has never been observed with as much intensity or in so many vibration modes as in our work. It can be attributed to changes in the resonance parameters (e.g., energy, number of decay channels and lifetime) in the condensed phase that affects the intensity of vibrational decay channels. The 2.5 eV feature can be assigned to a low-lying ${}^2A''_2$ shape resonance state with a large autodetachment width.^{40,47,48}

At the theoretical level, Trevisan *et al.*⁴⁹ reported a ~ 3 eV-wide resonance at about 8.6 eV in their momentum transfer cross sections. Trevisan *et al.* concluded that this structure is produced by two overlapping shape resonances of A_1 and B_2 symmetry. However, it is possible that these two resonances could be more separated in energy and correspond to those observed in this present work at 4.5 and 9.5 eV (Fig. 3). Furthermore, Winstead and Mckoy⁵⁰ calculation showed two resonances at 10 and 15 eV in the static-exchange approximation and when the polarization effects were included, the transient anion states were shifted downwards to about 8.3 and 13 eV. These energies are close to those in regions 3 and 4 of Table III. However, full inclusion of target relaxation could further downshift the theoretical energies. Two resonances at 8.6 and 14.1 eV were also found by Tonzani and Greene.⁵¹

Table IV shows a summary of the assignment of resonances character made by the various authors. The 2.5 eV maximum cannot involve electronic excitation and thus we can ascribe this structure to the formation of a shape resonance, as did Allan. Similarly, considering the broadness of the other features in our CSs data, they are expected to result from the formation of pure shape or core-excited shape resonances, in agreement with the assignments of Allan and all theoretical calculations. Feshbach resonances have lifetimes, which are usually longer than a vibrational period, and hence produce sharp (0.01–0.1 eV) features in scattering CSs;⁴⁴ thus, they are rarely seen in vibrational excitation functions,⁴⁰ recorded at large energy intervals, as in the present work. However, when the anionic state is dissociative, it has a broad Franck–Condon width and can easily be observed in the DEA channel. According to the arguments of Antic *et al.*,²⁶ core-excited shape resonance can also contribute to DEA. These authors ascribe the maximum at ~ 10 eV found in the electron-stimulated desorption of H^- to selective dissociation of endocyclic α -CH bonds via DEA.^{26,27}

V. SUMMARY

We reported absolute vibrational CSs for electron impact on condensed THF molecules. THF is a convenient model for deoxyribose, the sugar in the backbone of DNA. For each vibrational excitation mode of THF, an energy-loss spectrum was recorded from the scattering of 1–19 eV electrons from 1 ML of THF deposited on an inert Ar substrate

condensed on a polycrystalline Pt surface. The absolute values of the CSs were obtained from deconvolution of the vibrational peaks, calibration of the incident current and estimation of THF coverage onto the Ar spacer layer. These CSs were found to lie within the 10^{-17} cm² range. The measurements of both vibrational frequencies and resonance energies compare favorably to those reported by other groups, using electron and optical spectroscopies.

The electron-energy dependence of the CSs exhibits a common broad maximum at ~4.5 eV, a 2nd weaker structure at 9.5 eV and an even weaker one at 12.5 eV. These resonant features are in agreement with other experiments and in qualitative agreement with theory. Another resonance was found at about 2.5 eV. Although this maximum was not observed in theoretical studies, it can be compared to the resonance originally found in cyclopentane and in the work of Allan,⁴⁰ who also observed this enhancement experimentally in the vibrational excitation functions of gaseous THF. It is particularly interesting to note that new calculations by Curik *et al.*⁵² have recently predicted a resonance at about 2.5 eV in the ν_2 vibration mode of the closely related cyclopropane molecule and have confirmed the original symmetry assignment. The low-energy feature (2.5 eV) is attributed to the formation of a shape resonance and the others (4.5, 9.5, and 12.5 eV) to the formation of shape or core-excited shape resonances. The 9.5 eV resonance may be related to the fragmentation of THF leading to the production of H⁻ via DEA.^{26,27} In future experiments, it would be interesting to determine, not only absolute electronic excitation CSs for THF but also the absolute CSs for electronic and vibrational excitation of the entire deoxyribose molecule or other longer deoxyribose analogues, such as 3-hydroxytetrahydrofuran or α -tetrahydrofurfuryl alcohol, in order to move closer to biological reality.

Acknowledgments

This research was supported by a CIHR grant (No. MOP 86676). Thanks are extended to Mr. Marc Michaud for his valuable assistance and suggestions in the experimental phase of this project.

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FIG. 1.

Representative EEL spectrum obtained with electrons impinging with an energy E_0 of 7.5 eV on 1 monolayer (ML) of THF deposited on a 3 ML spacer film of Ar. The thin solid line passing through the data points is the sum of multiple Gaussian functions shown below, which fit the different vibrational peaks. The energies and widths of all features are listed in Table I. The horizontal dashed line accounts for the background scattering contribution from the Ar spacer and the Pt substrate.

FIG. 2.

EEL spectra for 1 ML of THF deposited on 3 ML of Ar on Pt at 20 K, recorded at the indicated electron impact energies (E_0). The thin solid line passing through each spectrum results from the fit of multiple Gaussian functions to delimit each vibration band, as shown in the bottom of the figure on the left side. The dashed line corresponds for the background contribution due to the Ar spacer and Pt substrate.

FIG. 3.

Variation with electron impact energy of the cross sections for various vibrational modes of THF. The values of the cross sections that result from the multiple Gaussian functions fits of energy-loss spectra are given in Table II. The vertical error bars result only from an uncertainty in the Gaussian fitting of about $\pm 10\%$.

TABLE I

Energy (meV) of vibrational modes in solid THF from Raman and infrared spectroscopic data, compared to those obtained by analysis of the present HREEL spectra of condensed THF.

Mode	Description	Optical spectroscopy ³⁸	Electron energy loss (this work)	FWHM
ν_{33}	Ring pucker + β -CH ₂ twist	17	17	27
ν_{17}	Ring pucker	37	37	35
ν_{32}	Ring bend + β -CH ₂ rock	73	73	21
ν_{16}	Ring bend	83	81	21
ν_{15}	β - and α -CH ₂ rock	104	102	31
ν_{13}	C $_{\beta}$ C $_{\beta}$ stretch + C $_{\alpha}$ C $_{\beta}$ sym. stretch	115	114	21
ν_{28}	C–O–C asym. stretch	131	131	21
ν_{10}	β -CH ₂ twist + β -CH ₂ wag +...	147	146	21
ν_{26}	β - and α -CH ₂ twist	155	156	21
ν_8	β -CH ₂ wag + β -CH ₂ twist	163	163	21
ν_6	β -CH ₂ bend	183	181	21
ν_5	α - and β -CH ₂ bend	187	187	40
ν_4	α -CH ₂ sym. stretch	357	357	21
ν_2	α -CH ₂ asym. Stretch	366	371	21

TABLE II

Cross sections $\sigma(10^{-17} \text{ cm}^2)$ for vibrational excitation by electron impact of 1 monolayer of THF on an inert Ar spacer at different energies E_0 (eV).

Vibrational modes										
E_0	σ	ν_{13} (114 meV)	ν_{28} (131 meV)	ν_{10} (146 meV)	ν_{26} (156 meV)	ν_8 (163 meV)	ν_6 (181 meV)	ν_5 (187 meV)	ν_4 (357 meV)	ν_2 (371 meV)
1.5	0.75		0.71	0.49	0.42	0.29	0.47	0.96	0.55	1.4
2	0.86		0.69	0.43	0.58	0.19	0.61	0.72	0.54	1.5
2.5	1.1		1.1	0.65	0.79	0.35	0.93	0.90	0.82	2.0
3	0.86		0.85	0.62	0.51	0.37	0.81	0.55	0.85	1.3
3.5	1.1		1.2	0.71	0.87	0.36	1.1	0.50	1.1	1.5
4	1.5		1.7	1.0	1.2	0.55	1.6	0.49	1.4	1.9
4.5	1.8		1.9	1.4	1.1	0.84	1.7	0.67	1.6	2.2
5	1.6		1.7	1.3	0.88	0.86	1.5	0.54	1.5	1.8
5.5	1.7		1.6	1.2	0.77	0.95	1.3	0.76	1.1	2.0
6	1.5		1.6	1.1	0.66	0.89	1.3	0.25	1.3	1.3
6.5	1.7		1.1	1.1	0.87	0.93	1.3	0.63	1.3	1.8
7.5	1.3		0.90	0.77	0.42	0.74	0.82	0.40	0.81	1.2
8.5	1.2		0.80	0.70	0.28	0.70	0.60	0.44	0.74	1.1
9.5	1.2		0.74	0.60	0.40	0.54	0.65	0.32	0.73	1.1
10.5	0.92		0.53	0.46	0.40	0.39	0.63	0.16	0.63	0.83
11.5	0.69		0.40	0.47	0.22	0.48	0.52	0.15	0.53	0.56
12.5	0.65		0.40	0.46	0.24	0.46	0.58	0.27	0.50	0.42
13.5	0.36		0.25	0.32	0.11	0.33	0.40	0.12	0.29	0.24
14.5	0.28		0.23	0.23	0.13	0.26	0.30	0.20	0.21	0.20
16.5	0.19		0.13	0.16	0.07	0.16	0.21	0.10	0.11	0.10
18.5	0.17		0.12	0.12	0.09	0.12	0.17	0.14	0.06	0.09

TABLE III

Energies of resonances decaying in specific vibration modes of THF for energy regions 1–4, corresponding to the colored rectangles in Fig. 3.

Vibration modes	Energy of resonances in each region (eV)			
	1	2	3	4
ν_{13}	2.5	5.5	9.5	12.5
ν_{28}	2.5	4.5	9.5	12.5
ν_{10}	2.5	4.7	...	12.5
ν_{26}	2.5	4.3	10.0	12.5
ν_8	2.5	5.7	8.5	12.0
ν_6	2.5	4.5	9.8	12.5
ν_5	2.0	...	8.7	12.5
ν_4	2.5	4.5	9.2	12.5
ν_2	2.5	4.5	9.5	...

TABLE IV

Experimental and theoretical resonances energies of THF taken from different references.

Source	Method	E _r (eV)	Character
Gas phase			
Lepage <i>et al.</i> ¹⁸	EEL excitation functions	8.4	Core-excited
Zecca <i>et al.</i> ³⁹	Transmission	7.5	Shape
Allan ⁴⁰	EEL excitation functions	6.2	Shape
Allan ⁴⁰	EEL excitation functions	10.8	Shape
Allan ⁴⁰	EEL excitation functions	2.6	Shape
Solid phase			
Lepage <i>et al.</i> ¹⁸	EEL excitation functions	4	Shape
Lepage <i>et al.</i> ¹⁸	EEL excitation functions	7.5	Core-excited
Lepage <i>et al.</i> ¹⁸	EEL excitation functions	10	
Antic <i>et al.</i> ²⁷	ESD of H ⁻	~10	Core-excited
Breton <i>et al.</i> ¹⁶	DEA yield of aldehydes	3.5	Shape
Breton <i>et al.</i> ¹⁶	DEA yield of aldehydes	12.5	Core-excited
Breton <i>et al.</i> ¹⁶	DEA yield of aldehydes	15	Core-excited
Breton <i>et al.</i> ¹⁶	DEA yield of aldehydes	18	Core-excited
Calculations			
Trevisan <i>et al.</i> ⁴⁹		8.6 (two overlapping resonances)	Shape
Winstead and Mckoy ⁵⁰		8.3	Shape
Winstead and Mckoy ⁵⁰		13	Shape
Tonzani and Greene ⁵¹		8.6	Shape
Tonzani and Greene ⁵¹		14.1	Shape