Absolute cross sections for vibrational excitations of cytosine by low energy electron impact

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Abstract

The absolute cross sections (CSs) for vibrational excitations of cytosine by electron impact between 0.5 and 18 eV were measured by electron-energy loss (EEL) spectroscopy of the molecule deposited at monolayer coverage on an inert Ar substrate. The vibrational energies compare to those that have been reported from IR spectroscopy of cytosine isolated in Ar matrix, IR and Raman spectra of poly-crystalline cytosine, and *ab initio* calculation. The CSs for the various H bending modes at 142 and 160 meV are both rising from their energy threshold up to 1.7 and $2.1 \times 10^{-17} \text{ cm}^2$ at about 4 eV, respectively, and then decrease moderately while maintaining some intensity at 18 eV. The latter trend is displayed as well for the CS assigned to the NH₂ scissor along with bending of all H at 179 meV. This overall behavior in electron-molecule collision is attributed to direct processes such as the dipole, quadrupole, and polarization contributions, etc. of the interaction of the incident electron with a molecule. The CSs for the ring deformation at 61 meV, the ring deformation with N-H symmetric wag at 77 meV, and the ring deformations with symmetric bending of all H at 119 meV exhibit common enhancement maxima at 1.5, 3.5, and 5.5 eV followed by a broad hump at about 12 eV, which are superimposed on the contribution due to the direct processes. At 3.5 eV, the CS values for the 61-, 77-, and 119-meV modes reach 4.0, 3.0, and $4.5 \times 10^{-17} \text{ cm}^2$, respectively. The CS for the C-C and C-O stretches at 202 meV, which dominates in the intermediate EEL region, rises sharply until 1.5 eV, reaches its maximum of $5.7 \times 10^{-17} \text{ cm}^2$ at 3.5 eV and then decreases toward 18 eV. The present vibrational enhancements, correspond to the features found around 1.5 and 4.5 eV in electron transmission spectroscopy (ETS) and those lying within 1.5–2.1 eV, 5.2–6.8 eV, and 9.5–10.9 eV range in dissociative electron attachment (DEA) experiments with cytosine in gas phase. While the ETS features are ascribed to shape resonances associated with the electron occupation of the second and third antibonding π -orbitals of the molecule in its ground state, the correspondence with DEA features suggests the existence of common precursor anion states decaying with certain probabilities into the vibrationally excited ground state.

I. INTRODUCTION

The passage of ionizing radiation into the cell nucleus leads directly and indirectly to DNA damage.¹ At the earliest time (i.e., $\sim 10^{-15} \text{ s}$), this damage is triggered by successive energy transfers (i.e., collisions) from the primary high-energy particles or other fast charged

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particles generated by them (e.g., Compton and photoelectrons) to the biological medium. Owing to the abundance of electrons in all matter and their light mass compared to the nuclei, these energy transfers consist essentially of electronic excitations and ionizations leading to production of positive ions, along with the ejection of secondary electrons (SEs).² Because the majority of these transfers involves relatively small energies (~20 eV),^{3–6} they occur in very large number (i.e., $\sim 5 \times 10^4/\text{MeV}$).⁷ Although excitations and ionizations may be comparable in numbers, substantially more energy flows into ionization.^{2, 8} It is for this reason that the ejected SEs, whose kinetic energies are distributed mostly from 0 to about 100 eV, carry most of the energy from the primaries.⁹ During the following stage, which extends from $\sim 10^{-15}$ to $\sim 10^{-12}$ s, these low-energy electrons (LEEs) deposit their kinetic energy within short ranges in the biological medium by producing nearby electronic excitations, ionizations, and temporary anions, before being thermalized or solvated. These secondary energy events along with those stemming from the primary particles lead to the formation of highly reactive cations, anions, and radical species. At the moment of their formation, these species can have kinetic energies much above the thermal energy and give rise to fast reactive scattering events. These events are followed by more conventional thermal chemical reactions. When the produced species arise from the DNA itself or from the most tightly bound water molecules,¹⁰ they contribute to the direct effect.^{11, 12} When they arise elsewhere, but subsequently attack DNA, they contribute to the indirect effect.^{11, 13}

LEEs are produced in very large quantities by ionizing radiation in presence of high-Z materials.^{14, 15} This latter characteristic becomes crucial in combined modality therapy using radiosensitizers, such as gold nanoparticles or platinum salts that bind to DNA, since an additional dose is delivered to DNA by an excess of LEEs having a range of only few nanometers. These LEEs generate a high density of energy deposits and clustered damage in the immediate vicinity of such radiosensitizers. Therefore, to carry out a dosimetry or more specifically a nanodosimetry in presence of these radiosensitizers requires the knowledge of the cross section (CS) for LEE to deposit their energy into the constituents of DNA.

Several experimental studies have been carried out on electron impact on individual DNA bases to know what are the fragments generated. Most of them concern the formation of various anion fragments produced by dissociative electron attachment (DEA) to these molecules in gas phase^{16–26} and sublimated as thin films.^{27, 28} Few studies have examined their electronic and vibrational excitations by electron energy loss (EEL) spectroscopy in the gas phase.^{29–31} So far, not much attention has been devoted on the determination of the *absolute* CS values for these different collision processes. The reason for this may lie in the low energy range where both experiments and theoretical calculations are difficult to perform. In line with these requirements, quantitative studies of the interaction of LEEs with DNA basis were undertaken recently by our group.³² More specifically, the *absolute* CSs for vibrational and electronic excitations of thymine,^{33–35} pyrimidine,³⁶ and adenine³⁷ by electron impacts have been measured over the 1–12 eV incident electron energy range for the molecules deposited at very low coverage on a solid Ar substrate. Besides the reported CSs, these studies showed selective vibrational enhancements at different electron impact energies, thus indicating the formation of several transient anion states. More recently, the *absolute* CSs to excite various electronic modes of cytosine by electron impact between 5

and 18 eV (hereafter referred to as paper I)³⁸ were determined for the molecule deposited at low coverage on an inert Ar substrate. The scattering model to extract the CSs was the same as in our previous work on pyrimidine³⁶ but the experimental method included some improvements. In contrast to our previous works, the EEL spectra at different incident electron energies and thus the electron impact energy dependences of the various CSs were obtained for exactly the same cytosine coverage on the inert Ar substrate. The end result was an important reduction of the scatter in the data. Besides, the cytosine coverage was calibrated directly in terms of *molecular number density* at the surface of the Ar substrate, thus avoiding the difficulty to recognize the monolayer coverage in the case of a disordered molecular deposit and further to assess its true value.

In the present paper, the *absolute* CS values to excite various vibrational modes of cytosine by electron impact between 0.5 and 18 eV are measured for the molecule deposited at low coverage on an inert Ar substrate. The experimental conditions (i.e., coverage, electron current, and electron exposure) to extract the vibrational CSs are exactly the same as those in paper I.³⁸ The present vibrational excitation energies are compared to those that have been reported from IR spectroscopy of cytosine isolated in Ar matrix,³⁹ IR and Raman spectra of polycrystalline cytosine,⁴⁰ and values that have been obtained from *ab initio* calculation.⁴¹ In general, the energy dependence of vibrational excitation CSs can be seen to exhibit from the excitation energy threshold a more or less steep rise followed by a monotonous decrease. This smooth behavior is explained by the dipole, quadrupole, and polarization contributions, etc. of the interaction of the incident electron with a molecule (i.e., direct processes).⁴² Some of the CSs, however, reveals enhancements around specific energies that are superimposed on the contributions due to the direct processes. The latter findings are discussed in terms of electron resonance processes reported from electron transmission spectroscopy (ETS) (Ref. 43) and DEA experiments^{21, 26} with gaseous cytosine.

II. EXPERIMENT

The measurements of the electron-scattering CSs were performed with a EEL spectrometer housed in a closed-cycle cryopumped UHV system at a typical base pressure of 5×10^{-11} Torr, as described in detailed previously.^{44, 45} Briefly, the incident electron beam on the sample is provided by a monochromator, which can be rotated from $\theta_0 = 14^\circ$ to 70° about the sample's normal, whereas the backscattered electrons are detected by an analyzer, which is fixed at $\theta_d = 45^\circ$ at the opposite azimuth. Double-zoom electron lenses at the exit of the monochromator and at the entrance of the analyzer allow focusing of the incident and analyzed electron beam on the sample over the energy range 0.1–50 eV. The samples to be studied are deposited on a metal substrate made of a 0.0075 mm thick polycrystalline Pt ribbon (Good-fellow Cambridge Ltd., 99.95%) having its two ends held mechanically to a ceramic disk. The latter is press fitted against the tip of the closed-cycle cryopump at 18 K thus providing a good thermal conductivity to cool the Pt substrate as well as electrical isolation. The Pt substrate is cleaned by resistive heating in UHV to a temperature of 1100 K for about 10 s. The EEL spectra presented in this paper were recorded with the monochromator oriented near to the normal to the sample at $\theta_0 = 15^\circ$ along with the analyzer fixed at $\theta_d = 45^\circ$. The combined resolution of the spectrometers was adjusted at 18 meV full width at half maximum (FWHM) for a transmitted current I_S of 0.26 nA, as

measured by an electrometer connected to the Pt substrate. The incident electron energy E_0 was calibrated, within ± 0.1 eV with respect to the vacuum level, by measuring with the electrometer the onset of the transmitted current.⁴⁶ The recordings were also obtained under sufficiently small electron exposures, so as to make sample decomposition and/or charging due to the trapping of electrons or creation of holes in the sample negligible. These effects were monitored by comparing the EEL spectra and the low-energy electron transmission onsets during the course of an experiment.

Gaseous and liquid samples to be condensed on the Pt substrate were initially prepared in a gas-handling manifold, which has been described in detail previously.⁴⁴ As in paper I, the amount of gas or vapor (P) admitted in UHV and deposited on the substrate was further converted to an absolute surface number density (n_S) using the relation $n_S = (2.04 \times 10^{14} \text{ cm}^{-2} \text{ mTorr}^{-1}) P$. The conversion factor is established from the P to grow a (111) monolayer of Ar (Matheson of Canada Ltd., 99.9995%) on the Pt substrate.^{47, 48} The uncertainty in the n_S value arises essentially from the error in the pressure measurement P at $\pm 2.5\%$ and the conversion factor at $\pm 7.5\%$ for a combined uncertainty of $\pm 10\%$.^{49–52}

Cytosine (Aldrich Chemical Ltd., 99%) was sublimated at a temperature of 90° under UHV condition with a double-stage oven system.³⁵ Since, it is generally accepted from vacuum ultraviolet,⁵³ photoelectron,⁵⁴ and IR (Ref. 39) spectroscopy studies that cytosine does not decompose upon heating up to 220°C in vacuum; the present sublimation temperature is expected to preserve the integrity of the molecule. Also, to prevent any insidious effect such as decomposition of the cytosine molecule by the Pt substrate, a 3-layer film of Ar was systematically used as a spacer.⁵⁵ Still as in paper I, the cytosine coverage was monitored *in situ* from the attenuation of the electron specular elastic reflectivity (i.e., $\theta_0 = 45^\circ$ and $\theta_d = 45^\circ$) from the underlying Ar substrate.³³ To obtain the cytosine coverage in terms of surface number density n_S , the attenuation of the specular elastic intensity was compared to that caused by a similar molecule pyrimidine (Aldrich Chemical Ltd., 99%), which was prepared in the gas-handling manifold. The attenuation of the specular intensity $I_R(P)$ was thus measured as a function of P of pyrimidine admitted in UHV and deposited on the substrate. From fitting the $I_R(P)$ data normalized to the value at $P=0$ (i.e., $I_0 R$) with the following relation, $I_R(P)/I_0 R = \exp(-P/P_0)$, the attenuation constant P_0 was deduced to be $0.873 \text{ mTorr} (\pm 2.5\%)$. Using the above conversion factor, the corresponding surface number densities n_S for P_0 was found to be $1.78 \times 10^{14} \text{ cm}^{-2} (\pm 10\%)$, which compares within the relative uncertainty to the values of 1.80×10^{14} and $1.62 \times 10^{14} \text{ cm}^{-2}$ for a single molecular plane along the [001] direction in the pyrimidine^{56–58} and cytosine crystals.^{59–61} For the present EEL measurements, the cytosine coverage was the same as in paper I with the normalized specular intensity $I_R(P)/I_0 R$ attenuated to about $0.31 (\pm 7.5\%)$. From above exponential relation this is equivalent to $P = 1.02 \text{ mTorr}$ with a relative uncertainty of $\pm 9\%$ arising from the relative errors in the normalized specular intensity at $\pm 7.5\%$ and P_0 at $\pm 2.5\%$. Finally, given again the above conversion factor, this yields a surface number density of $2.08 \times 10^{14} \text{ cm}^{-2} (\pm 16.5\%)$. Considering that similar values of 1.90×10^{14} and $2.17 \times 10^{14} \text{ cm}^{-2}$ have been obtained by scanning tunneling microscopy on Au(111) (Refs. 62 and 63) and molecular modeling based on van der Waals radii⁶⁴ for a monolayer of cytosine, the present value will be referred to for convenience as one-layer coverage. After several days of experiments, the sample holder and the electron spectrometer needed to be heated at about

50 °C during 48 h in order to remove the insulating deposits that deteriorate the measurements.

III. SCATTERING MODEL AND MEASUREMENT PROCEDURE

For an electron beam current I_0 of energy E_0 incident on a disordered molecular film deposited on an inert substrate, the scattering of electrons from the film can be described in terms of the multiple scattering theory developed previously.⁶⁵ However, when the thickness of the film is smaller than the electron mean free path, one may retain only the terms arising from single collisions within the film. Under this condition and for near normal incidence θ_0 , where electron scattering exhibits practically the cylindrical symmetry, it can be shown that the expression for the current of electrons measured by the analyzer in the backscattered direction θ_d after having transferred an energy $E - E_0$ into the film (i.e., EEL spectrum) reduces to³⁶

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

Here $I_0(\theta_d, E_0)$ is defined as an effective incident electron current. The latter may be seen as the portion of the incident electron current I_0 that would be backscattered into the analyzer in the same direction θ_d as the energy-loss spectrum $I(\theta_d, E_0, E - E_0)$ by a model material having a diffuse elastic reflectivity equal to one (i.e., all incident electrons being scattered out of the film).³⁶ In the present experiment, a value of 7400 counts s^{-1} eV ($\pm 7\%$) was obtained for $I_0(\theta_d, E_0)$ at $\theta_d = 45^\circ$ by depositing increasing amounts of pyrimidine or H_2O vapor on the Ar substrate and using the conservation law between the backscattered and transmitted current, as described in details previously.^{36, 66} Provided further that $I(\theta_d, E_0, E - E_0)$ and $I_0(\theta_d, E_0)$ at $\theta_d = 45^\circ$ represent the mean value of their respective θ_d angular distribution or else differ from their mean value in the same proportion, the quantity $\sigma_r(E_0, E - E_0)$ corresponds to a CS per unit energy transfer range for an electron of energy E_0 to deposit an energy $E - E_0$ in the film and be backscattered into the vacuum (i.e., differential CS integrated over the whole half-angular space in the backward direction).³⁶ The value n_s is the surface number density of molecules on the substrate corresponding to the thickness of the film. Finally, the factor $1/\cos \theta_0$ accounts for the projection of the incident electron beam section onto the film surface.³⁶

In practice several EEL spectra $I(\theta_d, E_0, E - E_0)$ are recorded for different E_0 in the direction θ_d on a sufficiently thin film. Given the above $I_0(\theta_d, E_0)$ along with n_s , the corresponding $\sigma_r(E_0, E - E_0)$ are deduced from Eq. (1). Each of the them are next fitted with multiple Gaussian functions to delimit the various excitation energy regions centered at about the energies $h\nu_i$ as

$$\sigma_r(E_0, E - E_0) = \sum_i a_i(E_0) \exp \left[-(E - E_0 + h\nu_i)^2 / b_i^2 \right], \quad (2)$$

with $b_i = \delta_i/[2(\ln 2)^{1/2}]$ and where $a_i(E_0)$ is the amplitude and δ_i the FWHM of a Gaussian function i .

Finally, the CS value to excite a molecule at about the energy $h\nu_i$ by electron impact is obtained from the area under the corresponding Gaussians distribution i , which is given analytically as

$$\sigma_{ri}(E_0) = a_i(E_0)b_i\pi^{1/2}. \quad (3)$$

In the case that an electron has the same probability to be scattered in the backward and forward direction with respect to the molecular film surface (i.e., isotropic scattering) $\sigma_{ri}(E_0)$ accounts for half of the integral CS.

IV. RESULTS AND DISCUSSION

A. Vibrational excitations

The cytosine molecule in its ground state, shown on the right side of Fig. 1, has a planar structure that contains all the atoms of the molecule, except for the two hydrogens sticking out of the amino group. Among the 33 vibrational modes, 23 are in the molecular plane.⁴¹ A survey vibrational EEL spectrum of a one-layer film of cytosine deposited on the Ar substrate is shown in Fig. 1. This spectrum results more specifically from averaging 12 different scans, which were recorded between $E_0 = 0.5$ and 6 eV. The overall EEL signal was found to be directly proportional to the amount of cytosine up to about one layer and then to saturate gradually toward higher film thicknesses. The latter behavior is due to the finite total electron mean free path in the bulk of a film and beyond which the molecules cannot be detected efficiently.⁶⁷ The large peak at zero energy loss corresponds to electrons scattered elastically from both the film of cytosine and Ar substrate. At higher energy loss and up to 450 meV, the energy-loss peaks are due essentially to excitation of various fundamental vibrational modes of the molecule. The thin continuous line superimposed on the spectrum results from curve fitting with multiple Gaussian functions to determine the various vibrational bands, as shown in the bottom of Fig. 1. The dashed line accounts simply for the background contribution due to the underlying Ar film and Pt substrate.⁶⁸ The energies and FWHM of all vibrational bands (i.e., Gaussians), which may include more than one fundamentals, are listed in Table I along with the reported excitation values obtained from IR spectroscopy of cytosine isolated in Ar matrix,³⁹ IR and Raman spectra of polycrystalline cytosine,⁴⁰ and *ab initio* calculation.⁴¹ Assignments of the vibrational modes are described as prescribed in Ref. 41, which follows the atom labelling of cytosine shown in the right side of Fig. 1.

In the very low energy-loss region, the quasielastic peak at about 26 meV stands for the two vibrational modes seen at 24 and 29 meV in IR spectrum of cytosine in Ar matrix. Both modes involve the molecular torsion with wagging of the C2-O8 bond. The two vibrational bands at 46 and 61 meV, whose sum results into an apparent shifting of the maximum toward lower energy loss with increasing E_0 , are assigned to the molecular torsion with C6-

H and N7-H symmetric wags at 41 meV and the ring deformation from the squeezing of the N3-C4-C5 group at 67 meV, as in the matrix experiment. From the comparison with the IR and Raman spectra of poly-crystalline cytosine, one may further consider the contribution from the symmetric bending of the C2-O8 and C4-NH₂ bonds observed at 66–68 meV in the polycrystalline experiments. As for the lack of minimum at 77 meV, it is attributed to the ring deformation with symmetric wagging of N1-H and C5-H bonds and wagging of the N7-H and N1-H bonds. These modes lie between 76 and 79 meV in the matrix experiment.

In the next energy-loss region, the maximum at 97 meV is ascribed to the ring deformation with symmetric wagging of the C5-H and C6-H bonds, as in the matrix and polycrystalline experiments. The following shoulder at 119 meV, which is not reported in the matrix case, concurs with the excitation bands ranging between 117 and 125 meV in both IR and Raman spectra of polycrystalline cytosine. These vibrational modes belong mainly to ring deformations with symmetric bending of all H and asymmetric wagging of the C5-H and C6-H bonds.

In the intermediate energy-loss region, the weak shoulder around 160 meV is ascribed, as in the IR spectrum of cytosine in Ar matrix, to the bending of all H at 154 meV and symmetric bending of the N1-H, C5-H C6-H bonds at 166 meV. The following shoulder at 179 meV corresponds to the scissoring of NH₂ with C4-NH₂ stretch along with symmetric bending of all H at 183 meV and deformation of the ring with bending all H at 176 meV. The strong peak at 202 meV agrees with the peaks at 198 and 205 meV both assigned to vibrational modes showing ring deformations from the C5-C6 stretch with NH₂ scissoring. Also in view of its energy-loss width, contribution from the C2-O8 stretch with ring deformation, which is observed at 206 meV in the IR spectra of polycrystalline cytosine, cannot be excluded. The lack of minimum at 142 meV is ascribed to various N-H bending modes ranging between 135 and 143 meV in the matrix and polycrystalline experiments.

In the high energy-loss region, the broad maximum at 382 meV is ascribed to both symmetric and asymmetric C5-H and C6-H stretching modes. Interestingly, these modes are observed exclusively in the Raman spectrum of polycrystalline cytosine at 379 and 386 meV, respectively. The weak shoulder at 355 meV, which is not seen in the IR spectrum of cytosine in Ar matrix, corresponds on the whole to several bands that have been reported between 332 and 363 meV (i.e., ~ 353 meV) in the IR spectra of crystalline cytosine in KBr. These bands have been attributed more specifically to the N1-H stretching mode for the molecules involved in strong hydrogen bonds, which in the present case would imply the existence of dimers at the surface of the Ar substrate. Finally, the broad maximum at 430 meV includes the symmetric and asymmetric vibrations of amino hydrogens (i.e., NH₂) found respectively at 427 and 442 meV in the matrix experiment. Still, the N1-H stretching mode found at 430 meV for the molecule isolated in the matrix (i.e., not involved in hydrogen bonds) is expected to contribute as well.

Besides the most prominent peaks, which are ascribed to the fundamental vibrations, one can see in Fig. 1 several weaker energy-loss features due to overtone and combination bands of some fundamentals. At sufficiently low molecular coverage plural scattering effect within a film is small and mostly overtone and combination bands may appear in a spectrum.

Furthermore, they appear generally at slightly lower energy than the resultant multiple losses. This can be seen for instance in Fig. 1 where the overtone observed at 751 meV is found at slightly lower energy than the double losses associated to the C5-H and C6-H stretching modes and which would have appeared at 764 meV (i.e., 2×382 meV) if the coverage had been higher.

B. Vibrational scattering cross sections

Vibrational EEL spectra of one-layer film of cytosine deposited on the Ar substrate were recorded for several incident energies E_0 from 0.5 to 6 eV in steps of 0.5 eV and from 7 to 18 eV in steps of 1 eV. Few representative spectra are shown as dotted curves in Figs. 2(a) and 2(b). The present intensity scale results from normalization to the effective incident current $I_0(\theta_{\text{el}}, E_0)$, as prescribed by Eq. (1). The thin solid line passing through the experimental data results from curve fitting with multiple Gaussian functions shown in the bottom of Fig. 2(a) and whose energy positions and FWHM obtained from Fig. 1 are given in Table I. These latter parameters, which define the various spectral regions pertaining to the vibrational excitations of cytosine, were kept fixed for all spectra, whereas only the Gaussian amplitudes were varied. As for the background signal present in each spectrum, it was simply taken into account by fitting with a broad Gaussian distribution (i.e., ~ 0.9 eV FWHM) centered at zero energy loss and decreasing to zero at the highest energy loss, as shown by the dashed line in the bottom of Fig. 2(a).

Since the contribution of elastic and multiple scattering to phonons from the underlying Ar film⁶⁸ cannot be easily removed from the elastic peak and vibrational bands of cytosine in the very low energy-loss region, only the CS for the vibrational excitations above 50 meV are presented in Figs. 3(a) and 3(b) and Table II. For each of the incident energy E_0 , the CS values were obtained by integrating over their corresponding Gaussian energy distribution and dividing by the molecular surface number density n_S (c.f., Eq. (1)). The error bars about the data points, which amount to $\pm 4.5\%$ on the whole, result only from the Gaussian curve fitting to the experimental spectra in Figs. 2(a) and 2(b). They do not include the systematic uncertainties arising from the calibration of the effective incident current $I_0(\theta_{\text{el}}, E_0)$ at $\pm 7\%$ and the determination of the molecular coverage n_S at $\pm 16.5\%$. Actually, the latter two values apply only to the vertical scale of Figs. 3(a) and 3(b). Hence, considering their sum at $\pm 23.5\%$ and the error bars; the total absolute error on the present CS values amount to $\pm 28\%$.

In Fig. 3(a), the CS for the ring deformation at 61 meV, the CS for the ring deformation with N-H symmetric wag at 77 meV, and the CS for ring deformations with symmetric bending of all H at 119 meV exhibit common enhancements around 1.5, 3.5, and 5.5 eV followed by a very broad maximum at about 12 eV. Yet, in the CS for the ring deformation with C-H symmetric wag at 97 meV, the 3.5-eV maximum appears at a slightly lower energy (i.e., 3 eV) along with the 1.5-eV enhancement seen more as a weak shoulder and the structure at 5.5-eV is completely lacking. The CSs for the various H bending modes at 142 and 160 meV are both rising from their energy threshold up to about 4 eV and then decrease moderately, while maintaining some value at 18 eV. The latter trend is displayed as well for the CS assigned to the NH₂ scissor along with bending of all H at 179 meV in Fig. 3(b). The CS for

the unresolved C-C and C-O stretches at 202 meV, which dominates in the intermediate energy-loss region, rises sharply up to 1.5 eV, reaches its maximum at 3.5 eV and then decreases up to 18 eV, while showing a hint of a shoulder at 5.5 eV and a broad hump at about 12 eV. The CS for C-H stretches at 382 meV rises up to 2.5 eV and then decreases reaching a small value at 18 eV. By comparison, the CS for NH₂ stretches at 430 meV is characterized by a steeper rise up to 2 eV and a relatively larger decrease reaching a very small value at high energy. Finally, the CS for the N-H stretches involved in hydrogen bonds at 355 meV is about an order magnitude smaller than those not involve in hydrogen bonds (i.e., 430 meV) in the first few eVs above the excitation energy threshold, and comparable in magnitude at higher energy (Table II).

It is most convenient to discuss electron collision with a molecule lying on a inert substrate in terms of direct⁴² and resonant processes^{69, 70} as in the gas phase. Direct process responsible for the excitation of the vibrational modes of a molecule results simply from the dependence of electron-molecule interaction potential on the corresponding coordinate. This interaction potential, which includes static-exchange and correlation effects, is described asymptotically by a single-center expansion into a dipole, quadrupole, and polarization terms, etc. Typically, the vibrational excitation CS that one calculates for each of these terms exhibits a smooth behavior of as a function of the incident electron energy E_0 .⁷¹ Among the present CSs, the energy dependence of the various H bending modes at 160 meV, C-H stretches at 382 meV, and NH₂ stretches at 430 meV, suggests that they arise essentially from direct process. More specifically, for dipole interaction (i.e., infrared-active mode) and for E_0 much larger than the vibration energy (i.e., $E_0 > 2$ eV) the electron energy transfer occurs mainly for small scattering angles and the energy dependence of the CS is predicted to fall off as $E_0^{-1} \ln E_0$.⁴² The steeper decrease of the present CS for the NH₂ stretches at 430 meV in Fig. 3(b), which is a strong IR absorption band in the matrix experiment, is further due to the kinematics of the electron-molecule collision.⁸ Under the current scattering angle of 120° (i.e., $\theta_0 = 15^\circ$, $\theta_d = 45^\circ$), the electron wave-vector transfer associated to a fixed energy transfer of 430 meV increases from 0.34 Å⁻¹ at the excitation energy threshold up to 3.74 Å⁻¹ at the incident electron energy E_0 of 18 eV. The same wave-vector transfer range would be achieved if E_0 was set to 200 eV and the scattering direction was varied from 2.7° to 30°. The CS for dipole interaction is strongly forward peaked at such incident energy and thus decreases with increasing scattering angle. This suggests that the present CS for an infrared-active mode should reach a maximum slightly above its excitation energy threshold and then decreases with E_0 more steeply than $E_0^{-1} \ln E_0$.

The presence of enhancements at specific energies in selective vibrational excitation CSs of a molecule is due to the formation of electron resonances or transient anion states during the collision of an electron with the molecule.^{69, 70, 72-74} An electron resonance occurs whenever an incident electron is captured temporally into an empty molecular orbital while the molecule is either in its ground or excited electronic state (i.e., parent state). For sufficiently long capture time (i.e., $\sim 10^{-12}$ – 10^{-14} s) and entirely repulsive anion state, the molecule can dissociate into an anion along with one or more neutral fragments (i.e., DEA) or else cleave. For a bonding potential-energy surface, DEA or cleavage may still occur, but for the transient anion formed into the repulsive part lying above the dissociation limit. For shorter capture time (i.e., $\sim 10^{-14}$ – 10^{-15} s), it may result an efficient displacement of the

nuclei prior to electron autodetachment and the molecule may be left vibrationally excited with the electron scattered with a reduced kinetic energy. As a result, the energy dependence of the CSs for vibrational excitations may exhibit one or more enhancements (i.e., resonances) that may be superimposed on the monotonously energy varying contribution from the direct process.

The electron energy dependence for production of several anion fragments have been observed for cytosine in the gas phase^{16, 19, 21, 22, 26} and in the condensed phase as multilayer films.²⁸ In the latter result only low mass fragment anions possessing sufficient kinetic energies to surmount the film-vacuum potential barrier of the image force have been detected. The measurement of the H^- , CN^- , and O^-/NH_2^- yields as a function of the electron impact energy, show resonance structures at about 9 and 20 eV, which are superimposed on a monotonous signal rise from about 12 eV. This rise is attributed to dipolar dissociation that results from excitation of a neutral electronic state dissociating into a stable anion and cation. In the gas-phase, many more fragment anions have been found below 12 eV impact energy, where essentially DEA is operative. Among these, the CH^- , $\text{C}_3\text{H}_3\text{N}_2^-$, C_3HN_2^- , OCN^- , CN^- , and O^-/NH_2^- fragments appear to be the most interesting with their energy dependent production yield showing resonances lying within the 1.5–2.1 eV, 5.2–6.8 eV, and 9.5–10.9 eV range.^{21, 26} The comparison between the first three DEA resonance ranges shown as shaded rectangles in Fig. 3 and the present enhancements around 1.5, 5.5, and 12 eV in a number of vibrational excitation CS suggests the existence of common precursor anion states decaying with certain probabilities into the vibrationally excited ground state. As for the vibrational enhancements at about 3 eV in the CS for the ring deformation with C-H symmetric wag at 97 meV, and 3.5 eV in the CS for the ring deformation with N-H symmetric wag at 77 meV, the ring deformations with symmetric bending of all H at 119 meV and the C-C and C-O stretches at 202 meV, they cannot be explained by the DEA measurements.

However, the low-energy ETS,⁴³ which has been performed for cytosine in the gas phase, reveals resonance features at about 0.32, 1.53, and 4.5 eV, shown as vertical bars in Fig. 3. They have been assigned more specifically to shape resonances with electron occupation of the first, second, and third π^* -orbitals of the molecule in its ground state, respectively. These molecular orbitals (MOs) being antibonding in character, the equilibrium position of the nuclei in the anion states is changed from that of the initial ground state. For a residence time comparable to or shorter than a vibrational period and after electron autodetachment, the nuclei are forced toward their initial equilibrium position in the ground state, thus causing vibrational excitations. Considering that shape resonances in the gas phase are shifted ~1 eV to lower energy by the electronic polarization in the condensed phase,⁷⁵ the resonance feature at 4.5 eV in the ETS may well explain the present enhancements around 3.5 eV in some of the vibrational CSs.

As mentioned in the Introduction, radiation dose delivery with concomitant administration of radiosensitizers (e.g., gold nanoparticles or platinum salts), which are incorporated into DNA of the cancer cells, requires the knowledge of the various CSs for LEEs to deposit their energy into different excitation processes of the DNA constituents. A physical quantity that enters dose calculation is the mean energy loss per unit pathlength in a medium of unit

molecular density, also called stopping CS.⁷⁶ The latter is defined as the product of the integral CS and the mean energy loss associated to an electron-molecule scattering process. Such parameters can readily be estimated from CS data for LEE scattering from cytosine. Let us first consider for simplicity the sum of the total CS to excite the various fundamental vibrational modes of cytosine in its ground state with a maximum of $4.5 \times 10^{-16} \text{ cm}^2$ at the incident energy of 3.5 eV. At this energy the sum of the CSs to excite the singlet and triplet valence states, which has been obtained under the same experimental conditions in paper I, is nearly zero but reaches a maximum of $5 \times 10^{-16} \text{ cm}^2$ at 9 eV and then decreases toward 18 eV. So the vibrational and electronic CSs are comparable in magnitude but at different incident energies. Furthermore in paper I, the sum of the CSs attributed to the ionization of the four highest occupied MOs (i.e., π_H , π_{H-1} , n_N , and n_O),⁵⁴ rises steeply from a very small value at 9 eV to a maximum of $8 \times 10^{-16} \text{ cm}^2$ at 13 eV and then falls toward 18 eV. So assuming further isotropic scattering along with a mean vibrational excitation energy of 0.15 eV, a mean electronic excitation energy of 6 eV, and a mean ionization energy of 11 eV, the stopping CSs for the vibrational excitation, electronic excitation, and ionization processes are found to be roughly 1.4×10^{-16} , 6×10^{-15} , and $1.8 \times 10^{-14} \text{ cm}^2 \text{ eV}$, respectively.

These large differences in magnitude for the stopping CSs of the various excitation processes show that different underlying physics governs the energy-loss process above and below the electronic excitation threshold. Above the excitation threshold, a LEE loses a relatively large amount of kinetic energy per collision through electronic excitation and ionization. Also, electrons produced by ionization add to the number of LEEs. Ions and electronically excited species formed by LEEs are often chemically active and cause significant changes in neighboring molecules. On the other hand LEEs with kinetic energy below electronic excitation thresholds lose a somewhat smaller amount of kinetic energy per collision through vibrational and phonon excitations. They are primarily responsible for producing vibrationally excited species as well as forming anions and radicals through DEA. While the latter products are known for their high reactivity,⁷⁷ some vibrationally excited molecular species, even those with a single quantum of excitation, react much faster than species in the vibrational ground state. Thermally excited species usually interact relatively slowly with the surrounding atoms and molecules through thermal chemical reactions, causing often milder consequences to the medium.

V. CONCLUSION

The vibrational excitation energies of cytosine deposited on an inert Ar substrate compare favorably to those that have been reported from IR spectroscopy of cytosine isolated in Ar matrix,³⁹ IR and Raman spectra of polycrystalline cytosine,⁴⁰ and values that have been obtained from *ab initio* calculation.⁴¹ The presence of a low-energy shoulder for the C-H stretching modes suggests the presence of some hydrogen bonding among the cytosine molecules, which implies the existence of a number of dimers at the surface of the Ar substrate. Considering that the π^* shape resonances are coupled and split in the dimers, as for example in the formic acid dimer where the splitting has been found to be about 0.5 eV,⁷⁸ such a splitting in the case of cytosine may contribute to the broadening of the resonance features in Fig. 3. The accuracy of the LEE scattering CSs was enhanced owing to the use of the same cytosine coverage on the Ar substrate for different incident energies and the

calibration of the coverage in terms of surface number density, as in paper I. Therefore, the present results can be compared on the same basis with the electronic and ionization CSs of paper I. Typically, the energy dependence of the vibrational excitation CSs exhibits from their excitation energy threshold a more or less steep rise followed by a decrease. This overall behavior in electron-molecule collision is attributed to direct processes such as the dipole, quadrupole, and polarization contributions of the interaction of the incident electron with a molecule. The CSs of some of them, however, reveal at specific energies several maxima superimposed on the contributions due to the direct processes. These selective enhancements compare to the features reported in the ETS (Ref. 43) and DEA (Refs. 21 and 26) experiments with cytosine in gas phase. While the ETS features are ascribed to shape resonances associated with the electron occupation of the second and third π^* -orbitals of the molecule in its ground state, the correspondence with DEA features suggests the existence of common precursor anion states decaying with certain probabilities into the vibrationally excited ground state.

The stopping CSs for the vibrational excitation, electronic excitation, and ionization of cytosine by LEE impact are found to be roughly 1.4×10^{-16} , 6×10^{-15} , and 1.8×10^{-14} cm² eV, respectively. Still, the large differences between the vibrational, electronic, and ionization contributions have to be weighted in dose calculation against the energy degradation spectrum of LEEs. The behavior of the latter is expected to show below the electronic excitation threshold a preponderance of secondary LEEs resulting from ionizing collisions in the medium. Although, the contribution of LEEs with their short ranges (~nm) is not required in the conventional dosimetry of fast primary particles in a macroscopic volume, such as an organ, the same is not true when considering dose and damage heterogeneities at the level of the cell nucleus, the chromosome, or the DNA. This situation is met, for example, when radiation dose is delivered with the concomitant administration of radiosensitizers of high-Z atoms that incorporate into DNA of the cancer cells (e.g., bromouridine and cis-platin). Under these conditions, the nanoscopic dose and the evaluation of DNA damage could both be underestimated in conventional dosimetry owing to the neglect of LEEs.

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FIG. 1.

Survey vibrational EEL spectrum of one layer of cytosine deposited on a three-layer spacer of Ar. This spectrum results from averaging the scattered intensities of 12 spectra recorded for incident electron energies between $E_0 = 0.5$ and 6 eV. The thin solid line passing through the spectrum results from curve fitting with multiple Gaussian functions to delimit the different vibration bands, as shown in the bottom of the figure. Their energy positions and widths are listed in Table I. The dashed line accounts simply for the background contribution due to the underlying Ar film and Pt substrate.

FIG. 2.

(a) Vibrational EEL spectra of one layer of cytosine deposited on a three-layer spacer of Ar shown for different incident electron energies E_0 from 1 to 5.5 eV and (b) from 9 to 18 eV.

With the present intensity scale, the integral of an elastic or inelastic feature can be expressed in terms of an absolute reflectivity. The thin solid line passing through each spectrum results from curve fitting with of the multiple Gaussians obtained in Fig. 1 by varying only their amplitudes (i.e., keeping their energy positions and widths fixed), as shown in the bottom of Fig. 2(a).

FIG. 3.

(a) and (b) Electron impact energy dependences of the cross sections to excite various vibrational modes of cytosine. The values of the cross sections resulting from fitting with multiple Gaussian functions are listed in Table II. Although a vibrational mode cannot be excited below its own vibrational energy in vacuum, the cross sections for vibrational modes below 250 meV were extrapolated for simplicity to zero at $E_0 = 0 \text{ eV}$ (i.e., the closest incident energy step), whereas those above were extrapolated to zero at $E_0 = 0.5 \text{ eV}$. The shaded rectangles represent the energy ranges of the core-excited electron resonances that have been observed in anion fragment yields in DEA experiments with cytosine in the gas phase (Ref. 21 and 26). The vertical bars represent the shape resonances that have been found by ETS of cytosine in the gas phase (Ref. 43).

Vibrational energies $h\nu_i$ (meV) of cytosine from *ab initio* calculation and optical spectroscopy (infrared and Raman) compared to the electron energy loss (EEL) spectroscopy of a submonolayer film of cytosine condensed on an inert argon spacer. Values within parentheses are the FWHM (meV) of the vibrational energy losses as obtained from the multi-peaks Gaussian fitting. The data in cm^{-1} have been converted to meV with the factor of $8.065 \text{ meV}^{-1} \text{ cm}^{-1}$.

TABLE I

Theory ^d		EEL		Infrared		Raman
Plane	Assignment ^b	DFT	Film ^c	Matrix ^d	Crystal ^d	Crystal ^e
Out	Tors molecule, wag C2-O8	17	{	24		20
Out	Tors molecule, S wag C2-O8, C4-NH ₂	24		26(21)	29	
In	A bend C2-O8, C4-NH ₂	42			53	43
Out	Tors molecule, A wag C6-H, N7-H	51			55	50
Out	Tors molecule, S wag C6-H, N7-H	51	46(21)	41	62	55
In	S bend C2-O8, C4-NH ₂	62	{		68	66
In	Def ring (sqz group N3-C4-C5)	66		61(21)	67	66
In	Def ring (sqz group C2-N3-C4)	69		71	74	74
Out	Wag N7-H	71	{	76	87	
Out	Wag N1-H	83		77(21)	79	94
Out	Def ring (wag group N3-C4-C5), S wag N1-H, C5-H	88		77		
In	Breath molecule	91		93	97	97
Out	Def ring (wag group N1-C2-N3), wag N1-H	92		101	102	100
Out	Def ring (wag group N3-C4-C5), S wag C5-H, C6-H	95	97(21)	97	98	98
In	Def ring (sqz group N3-C4-N7), S bend all H	110	{		120	120
Out	A wag C5-H, C6-H	115		119(28)	134	123
In	Def ring (sqz group N1-C6-C5)	118			125	125
In	S bend NH ₂	128	{	135	143	137
In	A bend N1-H, C5-H	137		142(21)	139	136

Theory ^a		EEL		Infrared		Raman	
Plane	Assignment ^b	DFT	Film ^c	Matrix ^d	Crystal ^d	Crystal ^e	Crystal ^e
In	Def ring (str N1-C2, C2-N3), bend all H	148		148	153	158	158
In	Bend all H	151		154	158	153	154
In	S bend N1-H, C5-H, C6-H	166	160(21)	166	169	169	168
In	Def ring (str N1-C6, N3-C4), bend all H	173		176	181	182	181
In	Sciss NH ₂ , str C4-NH ₂ , S bend all H of ring	183	179(21)	183	187	186	185
In	Def ring (str C4-C5), bend all H	185		191	191	191	190
In	Def ring (str C5-C6), sciss NH ₂	200		198	211	200	199
In	Def ring (str C5-C6), sciss NH ₂	202	202(28)	205	203	203	205
In	Def ring, str C2-O8, sciss NH ₂ , bend N1-H	206		213	206	206	210
In	Str N1-H (molecules involved in hydrogen bonds)		355(31)		~353		
In	A str C5-H, C6-H	386					379
In	S str C5-H, C6-H	390	382(33)				386
In	S str NH ₂	435		427		393	394
In	Str N1-H	436	430(40)	430		416	416
In	A str NH ₂	453		442	419	419	

^aCalculated results on cytosine from Ref. 41.

^bBend, bending; breath, breathing; def, deformation; sciss, scissoring; sqz, squeezing; str, stretching; tors, torsion; wag, wagging; A, asymmetric; S, symmetric.

^cThis work.

^dReference 39.

^eReference 40.

TABLE II

Cross section $\sigma_{Tf}(10^{-17} \text{ cm}^2)$ for vibrational excitations of cytosine by electron impact at different energies E_0 (eV). The assignments and FWHM of the Gaussian distributions corresponding to the vibrational bands are reported in Table I.

E_0	Vibrational energy $h\nu_i$ (meV)											430
	61	77	97	119	142	160	179	202	355	382		
0.5	2.00	1.57	1.72	1.69	0.57	0.92	1.01	2.56				
1	3.41	2.63	2.97	2.47	0.68	1.11	1.44	3.47	0.19	1.17	2.10	
1.5	3.62	3.08	3.63	3.35	1.25	1.75	2.13	5.11	0.29	2.44	3.42	
2	3.48	2.65	3.88	3.38	1.21	1.79	2.13	5.13	0.40	3.18	3.74	
2.5	3.59	2.61	4.21	3.81	1.30	1.92	2.31	5.33	0.57	3.65	3.64	
3	3.89	2.86	4.52	4.36	1.41	2.10	2.46	5.49	0.60	3.38	2.86	
3.5	4.02	3.05	4.41	4.54	1.52	2.17	2.61	5.66	0.82	3.46	2.77	
4	3.91	3.08	3.97	4.41	1.65	2.13	2.57	5.33	0.79	3.23	2.25	
4.5	3.77	3.01	3.55	4.19	1.73	2.11	2.57	5.15	0.90	3.06	2.09	
5	3.63	2.74	3.04	3.91	1.58	1.99	2.27	4.77	0.75	2.59	1.73	
5.5	3.51	2.71	2.90	4.06	1.55	2.06	2.22	4.65	0.72	2.53	1.53	
6	3.29	2.52	2.68	3.84	1.54	1.90	2.13	4.23	0.69	2.15	1.20	
7	2.99	2.05	2.77	2.59	1.26	1.77	1.76	3.33	0.70	1.70	0.90	
8	3.06	2.15	2.55	2.37	1.15	1.64	1.64	2.89	0.68	1.36	0.60	
9	3.51	2.22	2.48	2.14	1.03	1.43	1.45	2.58	0.57	1.13	0.51	
10	3.91	2.61	2.56	2.19	0.99	1.28	1.36	2.41	0.49	0.95	0.45	
11	4.84	2.90	2.88	2.29	0.97	1.24	1.25	2.37	0.41	0.81	0.40	
12	5.29	3.00	2.99	2.40	0.92	1.08	1.12	2.18	0.35	0.67	0.35	
13	4.90	2.94	2.88	2.31	0.87	1.02	1.06	2.03	0.32	0.60	0.32	
14	4.52	2.64	2.62	2.06	0.75	0.86	0.90	1.65	0.22	0.46	0.22	
15	4.34	2.26	2.33	1.75	0.60	0.72	0.70	1.36	0.14	0.34	0.16	
16	3.76	2.04	2.06	1.53	0.53	0.63	0.60	1.12	0.11	0.29	0.14	
17	3.40	1.78	1.86	1.32	0.45	0.52	0.49	0.89	0.09	0.22	0.11	
18	3.04	1.44	1.54	1.02	0.35	0.38	0.35	0.64	0.03	0.16	0.09	