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Carbon 1*s* photoelectron spectrum of methane: Vibrational excitation and core-hole lifetime

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The carbon 1*s* photoelectron spectrum has been measured for CH_4 at photon energies of 302, 320, and 330 eV and for CD_4 at 330 eV with an instrumental resolution about half the natural linewidth. These spectra have been analyzed to obtain vibrational spacings, vibrational intensities, and the lifetime of the carbon 1*s* core-hole state. The vibrational intensities vary with photon energy, in agreement with earlier results. At 330 eV, the observed Franck-Condon factors for both CH_4 and CD_4 can be understood only if anharmonic effects (consistent with the predictions of theory) are included. On the other hand, the vibrational spacings in CH_4 show no evidence for anharmonicity (in contrast with theoretical predictions). In CD_4 the observed anharmonicity in the vibrational energy spacings is about half of the predicted value, but the experimental and theoretical values differ only by an amount comparable to the experimental uncertainty. The measured values of the lifetime show a dependence on photon energy; this is attributed to failure of the theory of post-collision interaction to predict correctly the observed electron spectrum near threshold. At 330 eV, the measured Lorentzian lifetime, 93–95 meV, agrees with predictions of simple theory, but not with the prediction of more complete theory. It is also observed that there are systematic discrepancies between the observed line shapes and those predicted by the theory of postcollision interaction. [S1050-2947(99)02305-7]

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I. INTRODUCTION

Recent progress in the development of high-brightness, high-resolution x-ray sources at synchrotrons has made it possible to study features of x-ray photoelectron spectra that were not clear at lower resolution. Among these are (1) the effects of atoms that have only slightly different ionization energies even though they are chemically inequivalent, (2) the vibrational structure, and (3) the intrinsic line shape. The last of these reflects both the lifetime of the core hole and the interaction of the photoelectron with an Auger electron [postcollision interaction (PCI)]. Particular molecules where such information is important and useful are organic molecules having only a few carbon atoms, in which we can expect to clarify chemical effects on core-ionization energies and, possibly, on the inner-shell lifetimes. The simplest such compound is methane, CH_4, whose x-ray photoelectron spectrum has been the object of many investigations [1–8]. Methane is a prototype for illustrating some of the important aspects of inner-shell photoelectron spectroscopy and therefore provides a testing ground for our understanding of the various processes involved. By taking advantage of the high-brightness characteristics of the Berkeley Advanced Light Source combined with a high-resolution photoelectron spectrometer, we may be able to achieve a detailed understanding of vibrational structure, lifetime broadening, and postcollision interaction in this molecule.

Vibrationally resolved inner-shell spectroscopy of methane is of interest for several reasons. First, methane serves as a standard in gas-phase electron spectroscopy. Calibrations for x-ray photoelectron spectra have been based on vertical transition energies, that is, those corresponding to the centroid of a vibrational manifold. However, with detailed vibrational structure being observed at high resolution, calibrants are needed for adiabatic transitions. Second, the vibrational progressions in the core-ionization spectrum reflect the change in structure of the molecule when a core electron is removed. For methane the structural change is contraction of the CH bond, and the extent of the vibrational excitation is highly dependent on this change. The analysis of vibrational structure thus provides a stringent test of the ability of electronic structure theory to predict molecular structure.

In the simplest picture only one vibrational mode is to be expected—the totally symmetric CH stretching mode. In this case the vibrational spectrum should consist of a single series of well-resolved peaks. Models for vibrational potential energy surfaces and for calculation of Franck-Condon factors can thus be tested if the spectrum exhibits enough detail in the vibrational progression. Methane provided the first evidence for vibrational structure in an inner-shell photoelectron spectrum. This was reported in 1974 by Gelius [1], who used monochromatized aluminum $K\alpha$ radiation as an excitation source. In 1985 Asplund *et al.* [2] reported similar spectra but with better resolution—about 0.22 eV. The first spectrum obtained with synchrotron radiation was a measurement of zero-kinetic energy electrons at threshold by Heimann *et al.* [3]. Since 1996 there have been five reports of high-resolution spectra measured at the National Synchrotron Light Source at Brookhaven [4,5] and at the MAX-I facility at Lund [6–8]. In these measurements, the instrumental resolution was comparable to or greater than the intrinsic linewidth (about 95 meV, resulting from the finite lifetime of the core hole). The Advanced Light Source coupled with high-resolution electron spectrometers provides the opportunity to measure this spectrum with a resolution of about half the intrinsic width and, therefore, to obtain a clearer view of the vibrational structure.

Another aspect of inner-shell photoelectron spectroscopy that is of fundamental importance is the lifetime broadening of the peaks. Lifetime widths of $1s$ hole states for first row elements are expected to be between 50 and 250 meV, with carbon in the 60–120-meV range [9,10]. Measuring the lifetime width, which is the Lorentzian part of the peak shape, is complicated by such factors as instrumental resolution and postcollision interaction. Extracting the width from the data requires either very good instrumental resolution or a good understanding of the instrumental resolution function, as well as a good theory of postcollision interaction. As a result, reported linewidths vary widely and have large uncertainties. For methane [2,3,5] these range from 83 ± 10 meV [5] to 120 ± 10 meV [3].

Finally, we note that at low photon energies, the spectrum is strongly distorted by postcollision interaction. The extent of this depends on the lifetime, and, thus, the PCI line shape potentially provides information on the lifetime. However, extracting this information depends on the accuracy with which PCI theory can describe the line shape. At high energies, the intrinsic line shape approaches Lorentzian, and the extracted information on linewidth is less critically dependent on PCI theory. Comparison of the line shapes obtained at different energies provides insight into the reliability of this approach as well as into PCI theory itself.

Here we present results on the carbon $1s$ photoelectron spectra of CH_4 and CD_4 measured with resolution about half the natural linewidth. These results provide a clearer view than has been previously available of the phenomena discussed above, but the details leave significant questions unanswered.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

Carbon $1s$ photoelectron spectra of CH_4 were measured on Beamline 9.0.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratory at photon energies of 302 and 320 eV (March 1997), and 330 eV (January 1998), approximately 11, 29, and 39 eV above the carbon $1s$ threshold (290.707 eV [2]). That of CD_4 was measured only at 330 eV. As indicated above, the low-energy measurements are most strongly influenced by PCI, and, therefore, provide a test of PCI theory. In the high-energy measurements, on the other hand, the vibrational structure is more clearly resolved. In addition, the statistical accuracy of the high-energy measurements is sufficiently good that these spectra also provide information on PCI theory, even though the effect of PCI on the spectrum is small at these photon energies.

Beamline 9.0.1 receives its radiation from an undulator (U10) with a 10-cm period. It is equipped with a spherical-grating monochromator that is capable of a resolving power of 10^4. Photon absorption measurements to determine energy calibration and photon resolution were made in a parallel-plate ion-yield analyzer. Photoelectron spectra were measured in a spherical-sector electrostatic analyzer at the two lower photon energies, and with a Scienta SES-200 spectrometer at 330 eV.

The resolution of the monochromator was determined by measuring the photon absorption spectrum for CO near the $(1s \rightarrow \pi^*)$ resonance at 287.4 eV. Voigt function fits indicated Lorentzian components in satisfactory agreement with the value of 85 meV reported by others [11]. A Gaussian width of 39 meV was measured at the two lower photon energies, and 32 meV at 330 eV. Electron-analyzer resolutions were determined by measuring the photoelectron spectra of argon $3p$ electrons (spherical sector analyzer) and xenon $5s$ electrons (Scienta analyzer) at several photon energies. The resolution function of the spherical sector analyzer was not purely Gaussian, and a Voigt function was used to provide better fits. At 11 eV kinetic energy the full widths at half maximum, Γ, were $\Gamma_G = 27$ meV, $\Gamma_L = 11$ meV; at 29 eV kinetic energy they were $\Gamma_G = 34$ meV, $\Gamma_L = 11$ meV. The resolution function of the Scienta analyzer was slightly skewed and slightly flat topped compared to a Gaussian. It was accurately described by a function of the form $\exp[-Q(x-x_0)]$, where $Q(x)$ is a fourth-order polynomial. However, the difference between this shape and a Gaussian of the same width does not significantly affect the results of our analysis. The resolution due to the monochromator combines with that due to the electron spectrometer to give a resulting instrumental resolution of about 55 meV for the low-energy data and about 42 meV for the measurements at 330 eV.

The transmission of the Scienta analyzer as a function of electron kinetic energy was determined using the procedure developed by Jauhiainen *et al.* [12]. This involves measurements of the xenon $N_{45}OO$ Auger and xenon $4d$ photoelectron spectrum. From these results we conclude that under the conditions of our experiment the transmission varies nearly as the reciprocal of the kinetic energy that the electron has before it enters the analyzer. Since this is the expected behavior, we have assumed that the transmission of the spherical sector analyzer follows the same function. The spectra were corrected using this assumption, but the correction is small and makes little difference in the final results. The xenon measurements also provided a calibration of the energy scale of the Scienta analyzer. Comparing our measurements of the positions of the Auger lines with those given by Jauhiainen *et al.* gives agreement within 0.2%. Measurements of the position of the xenon $4d$ and $5s$ photoelectron lines as a function of photon energy show that the shift of position with change in photon energy is within 0.1% of the expected amount. The $4d$ spin-orbit splitting was found to be 1979(3) meV, in excellent agreement with the value of 1982(2) meV given by Ausmees *et al.* [13]. Thus, we can expect relative energies measured with the Scienta analyzer to be accurate to better than 0.2%. On the basis of measurements of the argon $3p$ photoelectron spectrum and its shift with photon energy, we conclude that the uncertainty in the calibration for the spherical sector analyzer is about 0.6%.

Data were taken in series of short runs. Each spectrum was inspected and adjustments were made for small drifts in the energy scale. The adjustments are of the order of 10 meV and are probably due to changes in the beam position between one fill and the next and to changes in charging of the gas cell with decay of photon beam intensity. After these

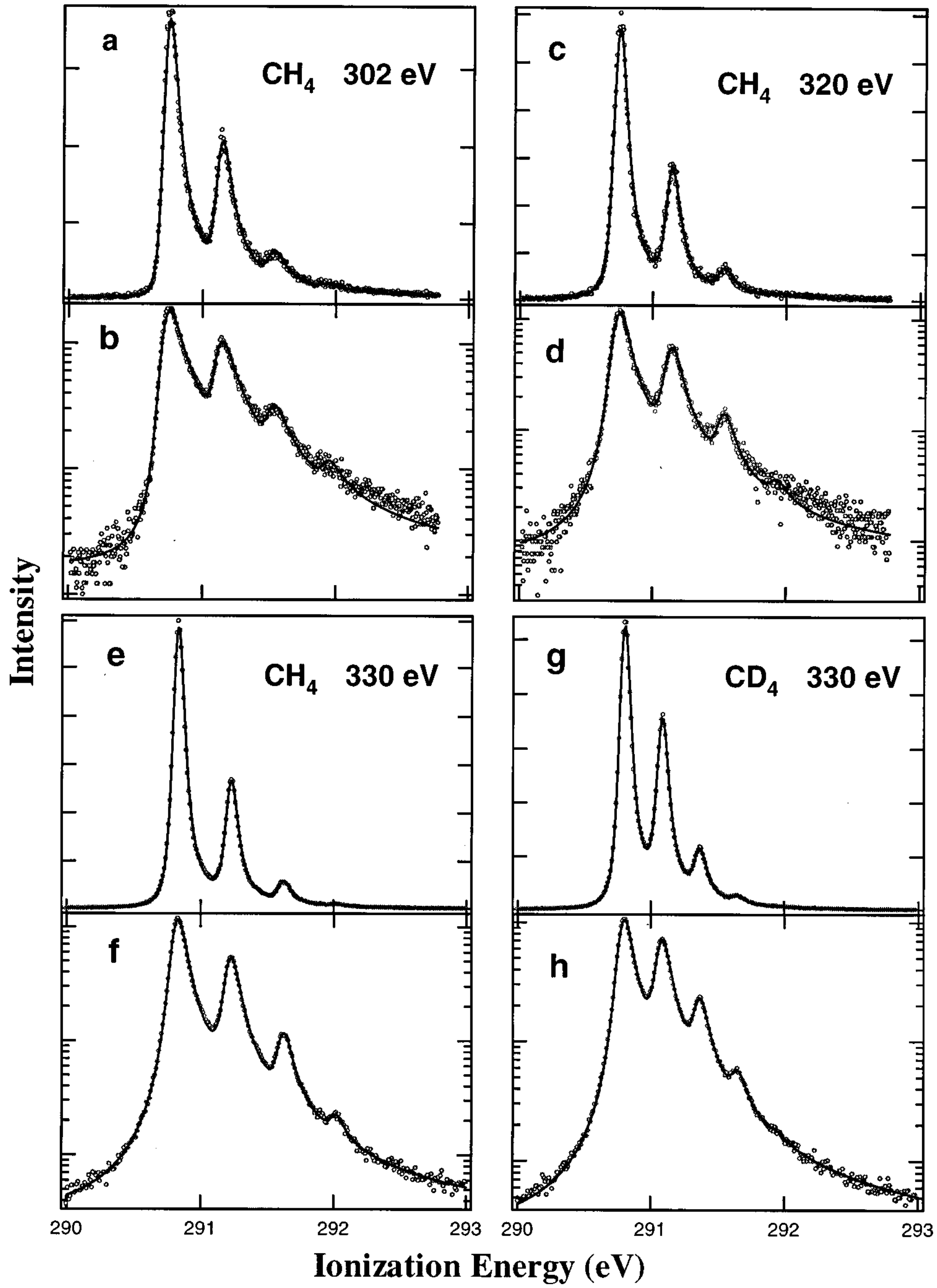

FIG. 1. Carbon 1*s* photoelectron spectra of methane at three photon energies. The solid lines show the results of least-squares fits to the data using the model described in the text. For each pair, [(a),(b)], [(c),(d)], etc., the data are shown on a linear scale (upper) and on a logarithmic scale (lower) in order to make clear the regions of agreement and disagreement between the data and the model.

adjustments, the data were combined to give a summed spectrum for each of the four experiments. The experimental results are shown in Fig. 1 as the circles. The solid lines represent least-squares fits to the data (discussed in the following paragraph). The data are shown on both linear and logarithmic scales to make clear the agreement and disagreement between the fits and the data in regions of both high and low intensity.

In the fits, the basic line shape is the PCI function of van der Straten, Morgenstern, and Niehaus [14], convoluted with the experimental resolution function and an additional Gaussian function to take into account the Doppler broadening. Fits using the function of Kuchiev and Sheinerman [15] were indistinguishable from those using that of van der Straten, Morgenstern, and Niehaus. For each fit, a value of the Lorentzian linewidth was chosen. Then a least-squares fitting procedure was used to fit four peaks to the CH$_4$ spectra and five peaks to the CD$_4$ spectrum. In these fits, the adjustable parameters were a constant background, the energy position and intensity of the $v=0$ peak, and the positions and intensities of the other peaks relative to the main peak. The points were weighted according to the reciprocal of the standard deviation of each point. This procedure was repeated for different choices of the Lorentzian width to determine the value that gives the lowest value of χ^2. Inspection of Fig. 1 shows that, for the most part, the agreement

TABLE I. Linear and quadratic fitting parameters to the observed vibrational splittings (meV).

	Photon energy (eV)	Fundamental[a] ν_1	Quadratic fit[b] Linear	Quadratic fit[b] Quadratic
CH_4	302	396.0 (2.5)	393.1 (1.3)	1.2 (0.8)
	320	393.2 (2.5)	392.8 (1.8)	0.2 (1.2)
	330	397.1 (0.9)	397.1 (1.2)	0.03 (0.5)
CD_4	330	284.2 (0.7)	284.9 (0.7)	−0.4 (0.3)

[a] The fundamental is the difference between the energies of the $v=1$ and 0 states. Uncertainties (shown in parentheses) include the uncertainty in the calibration of the energy scale of the electron spectrometer.

[b] Uncertainties reflect only the statistical uncertainty of the least-squares fit.

between fit and data is quite good. However, there are consistent systematic deviations that we see here and in the analyses of spectra for other molecules. These are discussed in a subsequent section.

III. RESULTS AND DISCUSSION

The essential results that come from this analysis are the positions, intensities, and Lorentzian widths of the peaks. These are presented and discussed in the following sections.

A. Line positions and anharmonicity

To allow for the possibility that the vibrational motion in core-ionized methane is anharmonic we have fit the positions of the peaks with a quadratic function of $v+\frac{1}{2}$, where v is the quantum number of the symmetric stretching mode. The important results of this analysis are shown in the last column of Table I, which gives the coefficient of the quadratic term. On physical grounds, we expect this coefficient to be negative, since this is the usual effect of anharmonicity. Only for CD_4 do we see a negative coefficient, −0.4 meV, and this is nearly within the experimental uncertainty of zero. The results for CH_4 can be compared with the corresponding quantities measured or calculated for the neutral molecule: −1.4 meV [16], −1.7 meV [17], and −1.5 meV [18]. For the core-ionized molecule, previous measurements indicate a value of −5 meV [2], ‘‘no conclusive sign of anharmonicity’’ [6], ‘‘some evidence for anharmonicity, although the effect is too small to be quantifiable’’ [5]. Calculations give values of −1 to −1.5 meV [2] and −2.4 meV [19]. Our results are inconsistent with a value as large as these. For CD_4, the anharmonicity for the neutral molecule is smaller, −0.68 meV [16] and −0.77 meV [18]. Our experimental value for core-ionized CD_4 is about half of these values, but is just within the experimental uncertainty.

For comparison with theoretical calculations of vibrational frequencies, it is useful to consider the fundamental frequency for the vibrational mode, which is the difference between the energies of the $v=1$ and 0 vibrational states. These are summarized in Table I in the column labeled ‘‘fundamental.’’ The uncertainties quoted in this column include both the statistical uncertainty, given by the least-squares fit, and the uncertainty in the energy calibration.

The weighted average of the three results based on the linear fits for CH_4 is 396.6(8) meV. This is to be compared with values of 430(20) [1], 391(3) [2], 391(5) [6], 400(10) [7], 396(4) [4], 396(2) [5], and 390(20) [3]. As can be seen, there is excellent agreement between our value and the results reported recently by Köppe *et al.* [4,5].

Results of a number of theoretical calculations have been presented for the fundamental frequency of symmetric stretching mode in core-ionized methane. These include a value of about 0.42 eV from Meyer [17], and 402, 406, and 436 meV from Asplund *et al.* [2]. Some of these differ significantly from the observed value. The difference between the observed and calculated values for the transition energies may arise from incomplete treatment of the anharmonicity. For a polyatomic molecule, with several normal modes, the energy can be written approximately as

$$E=\sum_{r}(v_r+d_r/2)\omega_r+\sum_{r}\sum_{s\geqslant r}(v_r+d_r/2)(v_s+d_s/2)X_{rs}+\cdots,$$

where the v’s are vibrational quantum numbers and the d’s are the degeneracies for the vibrational modes [16]. The quantity ω_r represents the harmonic term for the rth mode and X is the anharmonicity tensor. The fundamental frequency of a given mode can be written as

$$\nu_r=\omega_r+2X_{rr}+\sum_{s\neq r}d_sX_{rs}/2+\cdots.$$

It is apparent that the fundamental frequency contains contributions due to the anharmonicity of all of the modes. For neutral CH_4 this correction is about −15 meV [18]. For an estimate for the core-ionized molecule, we use the calculations of Martin and Lee [20] for $NH_4{}^+$ and $ND_4{}^+$. These molecules are isovalent with CH_4 and CD_4 and have equivalent cores to these ions. To the extent that core-valence electron correlation can be ignored, we expect the vibrational parameters of the nitrogen-containing ions to be the same as those for the core-ionized molecules, provided that suitable adjustments are made for differences in mass. For the symmetric stretch, no adjustment is necessary. From their calculations the correction for $NH_4{}^+$ (and, hence, for core-ionized CH_4) is about −20 meV. This correction would bring some of the various theoretical values into closer agreement with the measured value. However, such an anharmonic correction does not seem to be compatible with our observation that X_{11} for core-ionized CH_4 is very small.

For $NH_4{}^+$, Martin and Lee give a best value of 401.3 meV for the fundamental of the symmetric stretch, in good, but not perfect, agreement with our value of 396.6 meV for

TABLE II. Intensities of the vibrational structure in core-ionized methane. Normalized to 1 for the $v=0$ transition. Uncertainties are shown in parentheses.

v	302 eV—CH_4	320 eV—CH_4	330 eV—CH_4	330 eV—CD_4
0	1	1	1	1
1	0.470(4)	0.438(4)	0.424(2)	0.618(3)
2	0.098(2)	0.083(2)	0.0748(9)	0.161(1)
3	0.022(1)	0.009(1)	0.0063(4)	0.0238(7)
4				0.0013(4)

core-ionized CH_4. For $ND_4{}^+$ their calculated fundamental frequency is 288.4 meV, again slightly higher than our experimental value of 284.2 meV for core-ionized CD_4.

Comparison of molecular geometry calculations for $NH_4{}^+$ and core-ionized CH_4 shows a greater bond length for the core-ionized molecule than for the nitrogen-containing species. Thus, the higher frequencies predicted for $NH_4{}^+$ and $ND_4{}^+$ than are found for core-ionized CH_4 and CD_4 may reflect a stronger bond in the one case than the other.

B. Franck-Condon factors

The vibrational progressions were analyzed by allowing the intensity of each peak to be an independent variable in the fitting procedure. The results are shown in Table II where we see that the vibrational structure changes with excitation energy. The average number of quanta of vibrational excitation falls from 0.46 at a photon energy of 302 eV to 0.39 at 330 eV. This variation has been noted by Köppe *et al.* [5], and our results are in agreement with theirs. Between the threshold and a photon energy of about 315 eV there are contributions to carbon 1*s* photoionization involving doubly excited states [5] and these influence the Franck-Condon factors. Above this energy, the relative intensities appear to be independent of energy, and we confine further discussion to our results at 330 eV.

At 330 eV, the average vibrational energy for CH_4 is 156 meV. This can be viewed as the energy associated with creating the core-ionized species with bond lengths that are appropriate to CH_4 in its ground state rather than to core-ionized CH_4. We expect this energy to be nearly the same for both isotopomers, and this is the case. The average vibrational excitation for CD_4 is also 156 meV.

A first approach to understanding the Franck-Condon factors is to assume the harmonic oscillator model. Since all of the relevant frequencies are known, the only unknown variable is the change in bond length between neutral methane and core-ionized methane. We choose this quantity so as to reproduce the ratio of the $v=1$ to 0 intensities in CH_4 and CD_4. The results of these calculations are compared in Table III with the experimental Franck-Condon factors. Also shown are the values of Δr that were derived in this way: $-4.94(1)$ pm for CH_4 and $-4.96(1)$ pm for CD_4. The agreement between the two is excellent and they are also in agreement with the typical values of about -5 pm that have been reported for this quantity [1,3,4,6]. Further inspection of the comparison, however, shows that the predicted intensities for $v>1$ are higher than is observed experimentally. For the $v=4$ peak of CD_4, the discrepancy is a factor of 10 and for the $v=3$ peak of CH_4 it is more than a factor of 3. This failure of the harmonic oscillator model to account for observed Franck-Condon factors has been previously noted for both methane and ethane [8].

An alternate approach using the harmonic approximation is to treat Δr as an adjustable parameter in fitting the spectrum. This gives -4.64 pm for CH_4. In this case the disagreement between experiment and calculation is spread over the entire spectrum rather than focused on the $v=2$ and 3 peaks.

Including the effects of anharmonicity in the calculations of the Franck-Condon factors produces much better agreement with experiment, even though our measurements of the energies provide little evidence for anharmonicity. For these calculations, we have used the values of X_{11} for CH_4 and CD_4 calculated by Lee, Martin, and Taylor [18] and for $NH_4{}^+$ and $ND_4{}^+$ calculated by Martin and Lee [20]. As noted above, it is expected that the ammonium ions will have about the same vibrational parameters as the core-ionized molecules. We have found that values of Δr of $-4.77(2)$ pm for CH_4 and $-4.76(1)$ pm for CD_4 give the best agreement with the measured Franck-Condon factors. A comparison of the calculated and experimental Franck-Condon factors is given in Table III, where we can see the general agreement. The calculated Franck-Condon factors for $v=3$ in CH_4 and $v=4$ in CD_4 are nearly within experimental uncertainties of the experimental values.

The value of Δr has been difficult to calculate theoretically with accuracy sufficient to predict the vibrational struc-

TABLE III. Comparison of experimental and calculated relative Franck–Condon factors for data taken at a photon energy of 330 eV. Uncertainties are shown in parentheses.

	CH_4			CD_4		
v	HO[a,b]	Expt.	AHO[a]	HO[a,b]	Expt.	AHO[a]
0	1	1	1	1	1	1
1	(0.424)[b]	0.424(2)	0.428	(0.618)[b]	0.618(3)	0.617
2	0.111	0.0748(9)	0.0717	0.218	0.161(1)	0.162
3	0.0225	0.0063(4)	0.0057	0.0574	0.0238(7)	0.0231
4				0.0124	0.0013(4)	0.0019
Δr, pm	$-4.94(1)$[b]		$-4.77(2)$	$-4.96(1)$[b]		$-4.76(1)$

[a] HO, harmonic oscillator. AHO, including anharmonicity.

[b] Δr chosen to fit the $v=1$ to 0 intensity ratio.

TABLE IV. Lorentzian widths derived from the methane core-ionization spectra.

	Photon energy (eV)	Width (meV)
CH_4	302	101.7
	320	97.5
	330	95.4
CD_4	330	95.0

ture in core-ionized methane. Reported hole-state calculations [2,17] for core-ionized CH_4 give values of Δr ranging from -4.1 to -5.6 pm. As has been noted elsewhere [8], an error of 0.5 pm leads to a predicted spectrum that is obviously wrong, and a calculation must be accurate to within less than 0.1 pm to predict the spectrum satisfactorily. New calculations for CH_4 by Karlsen and Børve [19], which include both valence correlation and core-valence correlation, give Δr equal to -4.81 pm, in excellent agreement with our value of -4.77 pm.

C. Lorentzian widths

The Lorentzian widths derived from fitting the four photoelectron spectra are given in Table IV. The statistical uncertainties given by the fitting procedure are, in each case, less than 1 meV. There is, however, an additional source of uncertainty arising from the function that is used to describe the effect of postcollision interaction on the line shape. If this function is inadequate, we might expect the results derived at different photon energies to differ. Possibly the results derived from CH_4 would differ from those obtained from CD_4, since the vibrational envelopes for these two molecules are different. We note, however, that there is excellent agreement between the values for CH_4 and CD_4 at a photon energy of 330 eV. Beyond this, although there is approximate agreement of all of the numbers, there appears to be a trend for increasing linewidth at lower energies. If we include the value of 120 meV measured by Heimann *et al.* [3] at the carbon 1*s* threshold, there appears to be a definite trend to greater width at lower excess energy. Although this trend might be interpreted as a change in lifetime with energy of the photoelectron, we believe that it results from a failure of the PCI function to describe accurately the shape of the observed electron spectrum at photon energies close to threshold. This failure might arise because of inadequacies of the model near threshold or because there are contributions to the experimental spectrum at low energies from other sources, such as secondary Auger decay. In some exploratory experiments, we have examined the argon $2p_{3/2}$ photoelectron spectrum at several energies from 5 to 80 eV above threshold. At the lowest photon energies, the observed spectrum is not described well by the model we have used here. Moreover, the best fits at low energy are with lifetime widths considerably larger than the reported values of about 120 meV [21]. At energies of at least 40 eV above threshold the argon spectra are well represented by the PCI function and the value of lifetime derived from fitting these higher-energy spectra is in accord with the accepted value. From this analysis, we conclude that our measurements of the lifetime width for methane at a photon energy of 330 eV might be higher than the true value by no more than 2 meV. We thus feel confident in concluding that the lifetime width for methane is between 93 and 95 meV. This value is to be compared with experimental values previously reported, which span a wide range: 107(10) meV [2], 120(10) meV [3], 83(10) meV [5]. The theoretically predicted value given by Coville and Thomas [9] and by Larkins [10], which is based on an approximate molecular orbital calculation, is 96 meV, in excellent agreement with our experimental value. Theoretical values of 75 meV, calculated by Hartmann [22] using a multicenter approach, and 116 meV, recently calculated by Larkins and McColl [23], are not compatible with our result.

D. The PCI function

The intrinsic shape of the photoelectron spectrum is determined by the natural lifetime of the core-hole state and the interaction of the photo and Auger electrons. Several models have been proposed to describe this shape [14,15,24–28]. Of these the most complete is that of Tulkki *et al.* [28]; it is, however, the least convenient for use in a fitting procedure. The treatments of Russek and Mehlhorn [27], van der Straten, Morgenstern, and Niehaus [14], and Kuchiev and Sheinerman [15] contain most of the important features of the process. Of these, that of Russek and Mehlhorn is not mathematically convenient, and that of Kuchiev and Sheinerman is not applicable if the photoelectron has zero energy. While that is not a constraint in the present situation, our need to consider this problem when it is a constraint [29] has led us to choose the formulation of van der Straten, Morgenstern, and Niehaus. Comparisons show that there are no significant differences between these three approaches in the energy regions of interest here.

The possibility that the chosen functional form fails at photon energies close to threshold has been mentioned in the discussion of lifetimes. Evidence for such possible failure can be seen in Figs. 1(b) (photon energy of 302 eV) and 1(d) (320 eV). At the high-ionization-energy region of the spectrum, we see that the data fall systematically above the calculated line. This behavior is in contrast to that seen in the higher-energy spectra, Figs. 1(f) and 1(h), where the data fall more or less equally on both sides of the line. This discrepancy may be the source of the apparent energy dependence of the natural linewidth. In order to minimize the distance between the points and the line, the fitting procedure assigns an erroneously large linewidth at low photon energies.

Even at a photon energy of 330 eV, close inspection of the data shows systematic discrepancies between the fit and the data. In Fig. 2 we reproduce Fig. 1(e), together with two regions magnified for more convenient viewing. At both the top of the peak and in the valley between two peaks the data fall consistently above the line [30]. No adjustment of the parameters of our fitting procedure will remove both of these discrepancies. Sharpening the peak (by assuming a narrower resolution function or natural linewidth) brings the points and line in agreement at the top of the peak, but worsens the agreement in the valley. Broadening the peak has the reverse effect. This problem is not unique to methane, but is apparent in a variety of spectra that we have fit using this procedure.

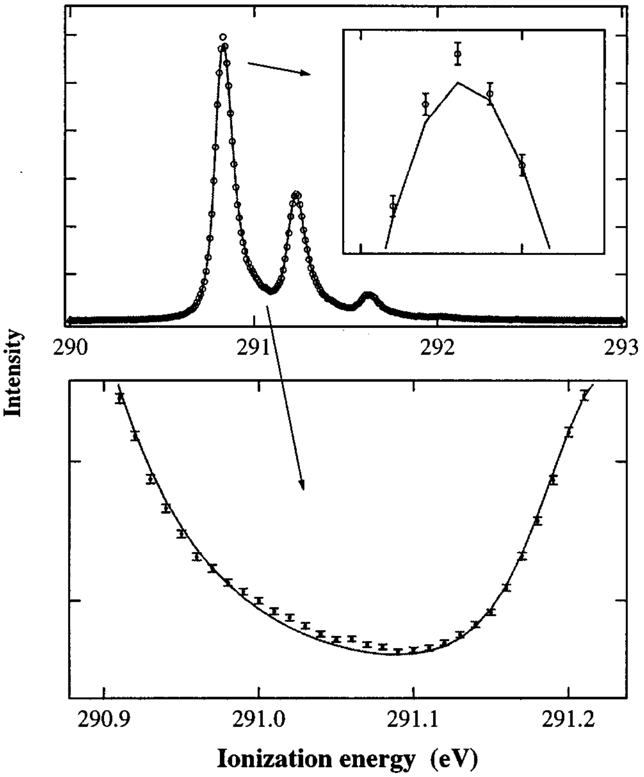

FIG. 2. Carbon 1*s* photoelectron spectra of CH_4 at 330 eV. The solid lines show the results of least-squares fits to the data using the model described in the text. Two regions of the spectrum have been magnified to show systematic discrepancies between the data and the model used to fit the data.

The theoretical model of van der Straten, Morgenstern, and Niehaus (and similar models by Russek and Mehlhorn and by Kuchiev and Sheinerman) describes the major features of the interaction between the photoelectron and the Auger electron well. However, detailed comparison shows disagreements between experiment and the model. It is possible that the more complete approach taken by Tulkki *et al.* [28] will resolve this discrepancy, but further consideration of this problem is beyond the scope of this paper.

IV. CONCLUSION

To first order, the core-ionization spectrum of methane is well understood. The vibrational frequencies and intensities are very close to what is predicted from *ab initio* theory. The line shapes are in approximate accord with the prediction of the theories of postcollision interaction and a reasonable value of the lifetime of the core-hole state.

To second order, however, there remain problems. First, the Franck-Condon factors for vibrational excitation of CH_4 and CD_4 at a photon energy of 330 eV are accounted for quite well by theory only if we include the effects of anharmonicity. On the other hand, the vibrational spacings seen for core ionization of CH_4 do not support an anharmonicity as large as that needed to account for the intensities or as large as that predicted by theory. Second, although the value of natural linewidth (93–95 meV) is in good agreement with approximate theory [9,10], it agrees badly with the recent and more careful calculations of Larkins and McColl [23]. Finally, we see that there are systematic discrepancies between the data and the prediction of theories of postcollision interaction. Although these are most apparent at low photon energies, there are still problems at the highest energies we have considered, 39 eV above threshold.

To shed further light on these problems, additional measurements at higher photon energies would be appropriate. At an energy 250 eV above threshold (the approximate energy of the Auger electrons) the postcollision interaction should vanish [31], and the intrinsic line shape should be Lorentzian. At this energy the Doppler broadening would be about 50 meV and is expected to be Gaussian.

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