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High-resolution C 1*s* photoelectron spectra of methane

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The C 1s partial photoionization cross section and photoelectron angular distribution of methane (CH_4) have been measured with high-energy resolution between threshold and 385 eV photon energy. From the analysis of the vibrational fine structure on the C $1s^{-1}$ photoelectron line a vibrational energy of 396±2 meV and an equilibrium bond length of 1.039(±0.001) Å for the $CH_4{}^+$ ion have been determined. The lifetime broadening was found to be 83(±10) meV. The weak feature in the photoabsorption cross section just above threshold does not influence the vibrational fine structure in a way typical for a shape resonance. We therefore suggest that it is due to doubly excited states of the type C $(1s)^{-1}(\mathrm{Val})^{-1}(\mathrm{Ryd})^1_a(\mathrm{Ryd})^1_b$, an assignment which is supported by recent Auger decay studies. Measurements of the shakeup structure revealed six satellite lines, one of which increases strongly in intensity at threshold, thus pointing to the existence of a conjugate shakeup process. [S1050-2947(96)08505-8]

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I. INTRODUCTION

The final state of a photoionized molecule may be characterized by a different equilibrium configuration compared to its neutral ground state. Since the time scale of the photoionization process is such that the nuclear coordinates remain essentially unaltered during the transition, vibrational fine structure is then expected to be visible in the photoelectron spectrum. Although this effect is well known in valence-level photoelectron spectroscopy, e.g., [1], the corresponding experiments in the core-level region have been difficult to perform with laboratory x-ray sources [2,3]. Recent studies on CO and N_2 using soft-x-ray undulator radiation have shown that variable photon energy and high spectral resolution are required in order to fully characterize such dynamic effects [4–6]. Of particular interest has been the perturbation of the vibrational fine structure at photon energies corresponding to the shape resonance, which in the valence region is also known to lead to non-Franck-Condon behavior, e.g., [7]. The effect is due to the dependence of the kinetic energy at which the shape resonance occurs on the internuclear separation: if a contraction occurs in the ion relative to the neutral ground state, the shape resonance will shift markedly to lower kinetic energies in higher vibrationally excited states. The reverse is also true, i.e., if the internuclear separation increases, the shape resonance will shift to higher kinetic energies. This shift in the resonance position has been shown to occur in the vibrationally resolved core-level photoelectron spectra of both CO [4,5] and N_2 [6].

For the purpose of comparison the molecule CH_4 is particularly interesting. Despite being polyatomic the C 1s vibrational fine structure is dominated by one vibrational mode (the symmetric C—H stretch) which, due to its high vibrational energy relative to the natural linewidth, can be well resolved [2,3,8,9]. There is, however, another reason: just above the photoionization threshold the total cross section of CH_4 shows a weak structure at about $h\nu = 303$ eV (labeled *a* in Fig. 1). It was first noticed in electron-energy-loss spectroscopy (EELS)-spectra [10] and thought to be an example of a (dipole-allowed) σ^*(C—H) shape resonance due to the backscattering of the outgoing photoelectron at the surrounding H atoms [11,12]. Piancastelli *et al.* pointed out, however, that the structure could be due to doubly excited states leading to satellite thresholds [13].

The possible existence of a shape resonance in the ionization continuum is closely connected to the question as to whether antibonding valence orbitals lie above or below the ionization threshold. Recent calculations have made it possible to examine the extent of mixing of valence and Rydberg excitations below threshold in CH_4 [14–16] and other hydrides [16]. Schirmer *et al.* concluded that while strong valence character was present in the $1s$-$np(t_2)$ Rydberg se-

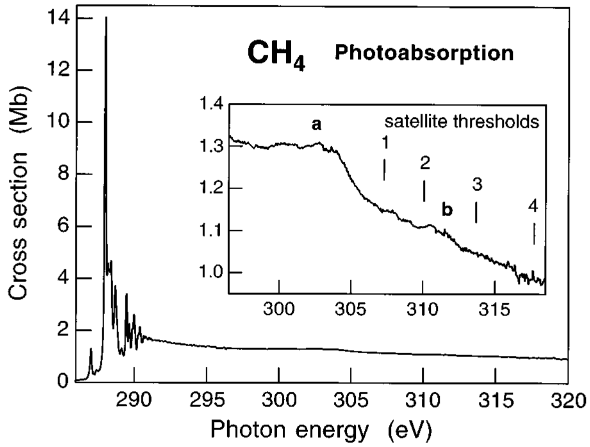

FIG. 1. Absolute high-resolution photoabsorption spectrum of methane (CH_4) measured in the C 1s threshold region [32]. Two structures labeled *a* and *b* in the figure are visible at photon energies of $\sim h\nu = 303$ eV and $\sim h\nu = 311$ eV, respectively. They are located several eV below the shakeup satellite thresholds (indicated by 1–4).

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ries, the $1s$-$ns(a_1)$ excitations were purely Rydberg, suggesting that a shape resonance associated with a C—H antibonding orbital could exist in the a_1 continuum. They pointed out, however, that although this might be the origin of the 303-eV feature, double excitations could not be excluded [16]. More recent calculations combined with an Auger decay study also indicate the little valence mixing takes place at all and thus support the assignment of the 303-eV structure in terms of a σ^* (t_2) shape resonance [17]. Vibrationally resolved photoelectron spectroscopy offers another approach to this problem, in that a careful study of the fine structure could assist in the identification of the continuum feature.

The C 1*s* shakeup satellite spectrum in CH_4 is also of some interest. In earlier experiments the satellite structure has been investigated directly at threshold using the zero-electron-kinetic-energy (ZEKE) method [9] and in the sudden limit [18,19] using Al $K\alpha$ radiation. In the latter study five satellite lines were observed, while only one broad structure, corresponding to the satellite with the lowest binding energy, occurred in the ZEKE spectrum. In some molecules, such as CO [4,5,20–23], CO_2 [24], and N_2 [6,21–23], conjugate shakeup processes are responsible for an increase in the intensity of certain satellites near threshold, while in other cases, such as H_2CO [25], C_2H_4 [21,25,26], and C_6H_6 [21,26,27], no evidence for such behavior has been found. The photon energy dependence of the CH_4 satellites has so far not been measured.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

The experiments were carried out on the high-resolution undulator beamline X1B [28] at the Brookhaven National Synchrotron Light Source x-ray ring. The photoelectron spectrometer was a stationary angle-resolving magic-angle cylindrical mirror analyzer (CMA). As described previously [29], it allows independent, simultaneous measurements of both the photoionization cross section and the angular distribution. The energy resolution of the spectrometer was set at ~120 meV (CMA pass energy: 15 eV) and that of the monochromator at ~100 meV (entrance slit width: 50 μm; exit slit width: 35 μm) for all main line photoelectron spectra. The overall resolution, as determined from the spectra, was ~150–160 meV. For intensity reasons satellite spectra were taken at a lower overall resolution of ~300 meV.

A least-squares-fit routine was used for the quantitative analysis of the vibrational fine structure; the individual lines were described by a convolution of three contributing profiles. The first important effect that has to be taken into account when measuring photoelectron spectra near the core-level ionization threshold is postcollision interaction (PCI), i.e., the interaction of the photoelectron with the subsequent Auger electron. When the slow photoelectron is overtaken by a fast Auger electron a transfer of kinetic energy takes place. The resulting PCI line shape shows a characteristic asymmetry and an energy shift which is negative for the photoelectron and positive for the Auger electron. Since a variation of the Auger electron energy leads to quite small effects, it can be well approximated by an average value deduced from the Auger spectrum. The fitting routine employs an analytical function for the PCI line shape derived by Armen *et al.* [30], which is based on the theory by Kuchiev and Sheinerman [31]. The second factor is the contribution of the CMA transmission to the skewness in the photoelectron line shape, as both trajectory calculations for the CMA and line shape measurements at different CMA pass energies have shown. This was quantitatively evaluated from measurements of the neon 2*s* photoelectron line at CMA pass energies and kinetic energies sufficiently high that PCI and contributions from the lifetime and from the monochromator could be neglected. The calculations as well as the experiments carried out confirmed that the transmission profile was practically constant for electron kinetic energies between a factor 0.5 and 2 of the CMA pass energy. Third, the monochromator profile leads to a symmetric Gaussian broadening of the lines as was determined from ray-tracing calculations of the beamline optics and from photoabsorption spectra of isolated narrow lines such as the $2p_{3/2}$-$4s$ transition in argon. The smooth background caused by secondary electrons could be well described by a heuristically derived exponential function near threshold as well as by a straight line at higher kinetic energies and was automatically subtracted in the fit.

A series of Ar 2*p* spectra [5] measured under comparable experimental conditions and in the same range of photoelectron kinetic energies as the C 1*s* spectra of CH_4 was taken as a test for the reliability of the above procedure. It became clear from the analysis of these data that even better results could be obtained by simultaneously fitting spectra measured at different photon energies, thus taking advantage of the systematic change of the PCI profile with photon energy. Some remaining uncertainty due to the incomplete separation of the contributions from the three different line profiles described above is responsible for the error given for the lifetime broadening, but has negligible influence on the determination of energy positions and relative intensities.

In summary, from this analysis partial photoionization cross sections, asymmetry parameters, the vibrational energy, and the lifetime broadening of the core hole state were determined. Absolute values for the cross sections were obtained by scaling to absolute photoabsorption measurements. (Note that in Fig. 1 the absolute cross section is plotted, which is only possible when the contribution of higher-order light from the monochromator has been effectively suppressed during the measurement [32].) The broad satellite lines were described by skewed Gaussian functions; a smooth background was subtracted in the fit.

III. VIBRATIONAL STRUCTURE

The high-resolution photoabsorption spectrum of CH_4 in the carbon *K* near-edge region is shown in Fig. 1. The spectral features below threshold are in agreement with previous high-resolution measurements [16,17,33,34] and will not be discussed further here. The continuum region is characterized by two broad structures *a* and *b* (see scale-expanded inset) at ~303 and ~311 eV, respectively. As noted in the introduction, *a* was first identified in EELS spectra [10] and thought to be a shape resonance, although it does not have the typical appearance of such a feature. It should be remembered, however, that multiply excited (neutral) states are often superimposed on shape resonances and could distort the observed profile. The structure *b* was also observed in the

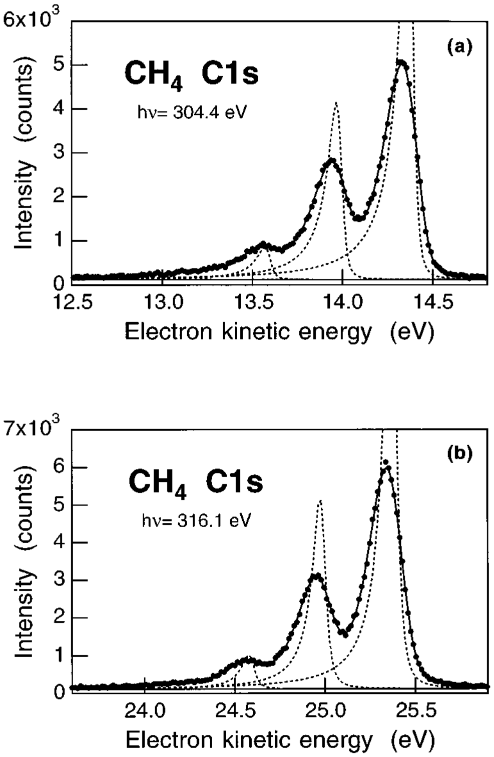

FIG. 2. C $(1s)^{-1}$ photoelectron spectra of CH_4 measured (a) on and (b) above the structure *a* at 303 eV. The results of a least squares fit are shown: the individual lines of the vibrational fine structure after summation and convolution with the instrument profiles give the full line through the data points.

EELS study, but has so far not been discussed in any detail.

Two C $1s$ main line photoelectron spectra taken at (a) the photon energy of the structure *a* and (b) at a higher energy are shown in Fig. 2. The deconvoluted vibrational fine structure shown as dashed lines graphically demonstrates the strong asymmetry of the spectral line shape due to the PCI effect which persists up to several tens of eV above threshold. The (harmonic) vibrational energy is found to be 396 (±2) meV compared to 361 meV in the neutral ground state [35]. In the $Z+1$ equivalent core model core-ionized CH_4^+ corresponds to valence-ionized NH_4^+ for which the ν_1 symmetric stretch has an energy of 421 meV [36], i.e., considerably higher. In the case of core-ionized CO^+ [5], for which valence-ionized NO^+ is the analogue, the agreement is better: 302 and 308 meV, respectively.

Previous measurements on CH_4 have yielded values of 391 (±3) meV for the vibrational energy using monochromatized Al $K\alpha$ [8] and 390 (±20) meV using the ZEKE method [9]. Both agree surprisingly well with the present, certainly more accurate determination. Asplund *et al.* [8] also found some evidence for anharmonicity, which is confirmed by the present study, although the effect is too small to be quantifiable. Above ~320 eV photon energy no further changes take place in the vibrational structure (see below), and it is possible to determine the equilibrium internuclear separation R_e in core-ionized CH_4^+ by performing a Franck-Condon analysis. This can be done either by directly calculating the Franck-Condon factors based on harmonic oscillator wave functions or by applying the approximation given by Nicholls [37]. In both cases the best agreement with experiment is found for $R_e=1.039$ (±0.001) Å, compared to $R_e=1.086$ Å in the neutral ground state [38,39]. The contraction in the C—H bond length is consistent with the increase in vibrational frequency. In Table I the present results as well as those of previous authors are summarized.

The analysis of the vibrational fine structure also gives a value of 83 (±10) meV for the core-hole lifetime broadening. Earlier experiments have given significantly higher values: 107 (±10) meV with Al $K\alpha$ [8] and 120 (±20) meV with ZEKE [9]. The lifetime broadening is lower in CO [C $1s^{-1}$, 78 (±10) meV [5]], but higher in N_2 [100 (±10) meV [6]]. The values calculated by Coville and Thomas [40] are 73 meV for CO, 96 meV for CH_4 (see also [41]), and 120 meV for N_2, which follow the same trend. The experimental values for CO and CH_4 are consistent with the expected influence of the chemical environment on the core-hole lifetime [40,41]: if the atom on which the core hole is located is bonded to a more electronegative atom, then the electron density around the core hole is reduced and the Auger decay rate is correspondingly lower. Hydrogen as a bonding partner is less electronegative than oxygen so that the Auger decay rate is expected to be higher, the lifetime shorter, and the broadening correspondingly greater in CH_4^+ compared to CO^+. Note, however, that the uncertainty in the two values (±10 meV) is greater than their difference (5 meV).

A comparison of the two photoelectron spectra in Fig. 2 shows very little difference in the vibrational fine structure at the two photon energies, which is in sharp contrast to the situation in CO [5] and N_2 [6]. In order to examine the influence of the structure *a* in more detail we plot in Figs. 3(a) and 3(b) the partial cross sections and asymmetry parameters

TABLE I. Comparison of present and earlier results for the vibrational spacing, the equilibrium bond length and the core-hole lifetime broadening of CH_4.

	Method	Vibrational energy (meV)	Equilibrium bond length, R_e (Å)	Core-hole lifetime broadening (meV)
Gelius [3]	Al $K\alpha$	430±20		
Meyer [45]	Theory	420	1.037	
Asplund *et al.* [8]	Al $K\alpha$	391±3	~1.036	107±10
Heimann *et al.* [9]	synchr. rad. (ZEKE)	390±20	1.033	120±20
This work	synchrotron radiation	396±2	1.039	83±10

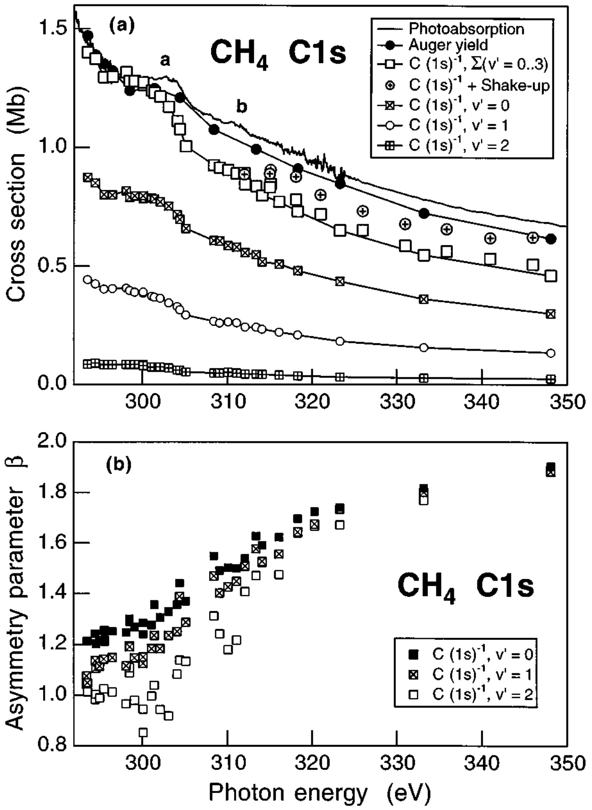

FIG. 3. The vibrationally resolved CH_4 C $(1s)^{-1}$ cross sections (a) and asymmetry parameters β (b) (for further details, including a discussion of errors, see text).

of the vibrational states $v'=0$, 1, and 2. Also shown in Fig. 3(a) is the C $1s^{-1}$ (single-hole) partial cross section (i.e., the summed intensity of all the vibrational lines included in the fit), the sum of the single-hole and shakeup cross sections, the total Auger yield (derived from Auger spectra measured in the same scan), and the complete C 1*s* partial photoionization cross section. The latter is obtained by subtracting the background due to valence excitation in the photoabsorption spectrum.

The scaling to the absolute C 1*s* partial photoabsorption cross section may involve some errors. Even the fitting of the total Auger yield to the photoabsorption cross section indicates that there are normalization problems: in Fig. 3(a) the Auger yield has been set equal to the photoabsorption cross section at low energies, but remains ca. 5% below its value at high energies. The other curves have been scaled such that the C $1s^{-1}$ single-hole cross section coincides with the Auger yield and photoabsorption cross sections near to threshold. In this region there are no satellites in the photoelectron spectrum and no double excitations. Realistically, we expect the absolute values of the various partial photoionization cross sections to have error bars of ±10%. We note that Rosi *et al.* [42] have published calculated partial cross sections and asymmetry parameters for the fluoromethane series $CH_{4-n}F_n$ $(n=0-4)$ using the $X\alpha$ SW method. Unfortunately, the agreement with the present results for CH_4 is rather poor.

The structure *a* is well reproduced in all the partial cross sections of the vibrational states; *b* also has some influence on the cross section, but because of its low intensity it is only visible in the sum curve. Supplementary to the cross sections in Fig. 3, the branching ratios of the intensities of $v'=1$ and $v'=2$ relative to $v'=0$ are plotted in Fig. 4, again showing how small the relative changes in the vibrational structure are. The striking difference in the behavior of *a* compared to the shape resonances in, for example, CO or N_2, is that there is no shift at all in its energy. According to the experience gained from previous work on shape resonances in valence-level (e.g., [1,7,43],) and core-level [4–6] photoionization, this is a very unexpected result. The experiment thus indicates that other processes are likely to be responsible for this feature. In analogy to CO and N_2, the position of *a* suggests that it might instead be due to doubly excited states. From the configuration of the neighboring shakeup satellites 1 and 2 [18] (see Fig. 1) a doubly excited state of the type $(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^1(\mathrm{Ryd})^1$ or $(1a_1)^{-1}(1t_2)^{-1}(3pt_2)^1(\mathrm{Ryd})^1$ might be expected at *a*. The presence of such a structure in the single-hole cross section is consistent with the situation in CO, CO_2, or N_2 where a strong coupling of doubly excited states to the C $(1s)^{-1}$ continuum was found. Further evidence for the existence of double excitations follows from a recent analysis of resonant Auger decay spectra [44] above and below threshold, enabling an accurate classification of the states. The structure *a* can be attributed to the configurations $(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^1(3pt_2)^1(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^2$, while *b* and some possible small features between *a* and *b* are most likely related to the satellites 3 and 4. The latter, following the assignment of the shakeup states by Creber *et al.* [18], probably correspond to the configurations $(1a_1)^{-1}(2a_1)^{-1}(3sa_1)^1(3pt_2)^1$ and $(1a_1)^{-1}(2a_1)^{-1}(3pt_2)^1(4sa_1)^1$.

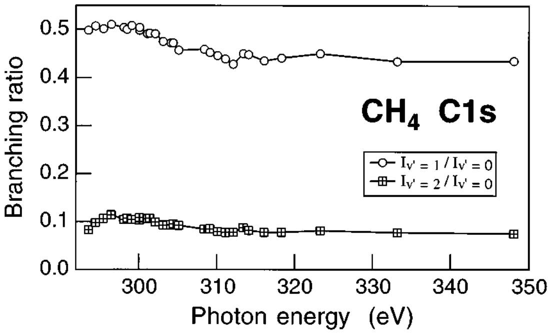

FIG. 4. Branching ratios for the different vibrational channels C $(1s)^{-1}$, $v'=1$ and C $(1s)^{-1}$, $v'=2$ showing the slight influence of the structure *a* at the same energy in both curves.

The asymmetry parameter curves are very similar for the vibrational states $v'=0,1,2$ [Fig. 3(b)], although β is somewhat smaller for excited vibrational states. Its value increases slowly from ≈1 near threshold to ≈1.9 at $h\nu=350$ eV. A broad oscillation, as is found around the shape resonances in CO and N_2, does not occur. On the other hand, there is an unexpectedly high scatter in the β values, especially between $h\nu=300$ eV and $h\nu=320$ eV. Since the quality of the data is such that noise should not be responsible for this effect, a possible explanation might be that the presence of many double excitations in this energy range causes strong distortions in the angular distribution.

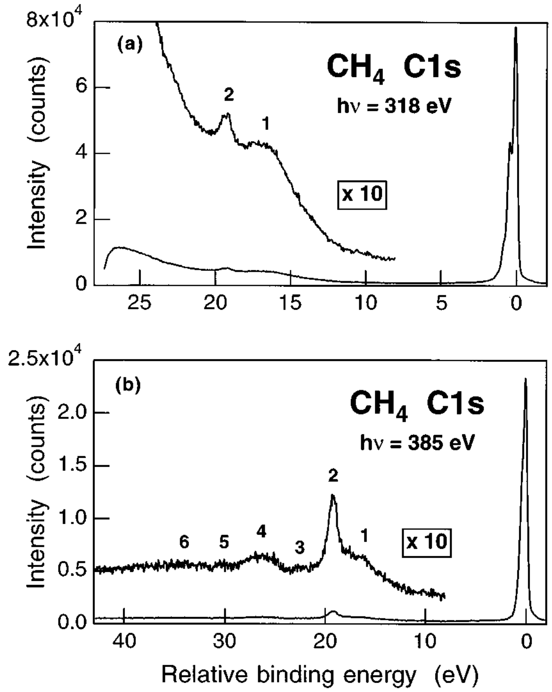

FIG. 5. C (1*s*) shakeup satellite spectra of CH_4. Towards threshold peak 1 shows a large rise in relative intensity, which points to the existence of a conjugate shakeup process.

IV. SHAKEUP SATELLITES

Shakeup satellite spectra measured at photon energies of $h\nu=318$ and 385 eV are depicted in Fig. 5. The background visible in the low-kinetic-energy region is caused by secondary electrons. The satellite peaks 1–4 and 6 were observed in Al $K\alpha$ measurements by Creber *et al.* [18] and Pireaux *et al.* [19]; satellite 5 has not been resolved hitherto. Table II gives an overview of the assignments made by Creber *et al.* as well as the various experimentally measured energies relative to the main line. The width of the peaks and the scatter in the data make it difficult to determine exactly the satellite thresholds. It is most likely that various states contribute to the broad bands, in particular to 1, 4, and 6. In Table II the widths and energies of the skewed Gaussians used to fit the structures are given. The separations of the satellite peaks 2–4 from the main line are in good agreement with earlier results; the somewhat higher separation of satellite 1 in the present work may be an indication that some of the states contributing to its profile are enhanced near threshold (see below). Due to the asymmetry of peak 6 only an approximate energy separation can be given.

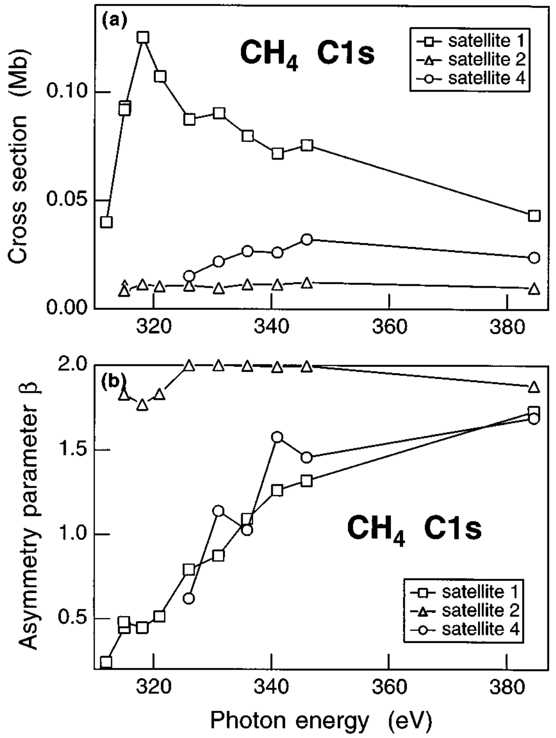

FIG. 6. (a) Partial cross section and (b) asymmetry parameter β for the most intense C 1*s* shakeup satellites 1, 2, and 4 of CH_4 in the threshold region.

The total intensity of the satellite features both in the sudden limit [18] and at $h\nu=385$ eV accounts for approximately 30% of the main line intensity, but the percentage slowly decreases as threshold is approached. At the same time the relative satellite intensities change, with peak 1 increasing drastically near threshold. The shakeup partial cross sections and asymmetry parameters are plotted in Fig. 6. For the sake of clarity only the most prominent satellite peaks 1, 2, and 4 are displayed in the figure. While the cross section of satellites 2–6 stays nearly constant, a very large increase occurs in the cross section of satellite 1; its intensity reaches a maximum at ~320 eV before decaying steeply close to the ionization threshold. For the satellites 1 and 4 the asymmetry parameter β [Fig. 6(b)] is very similar to that of the main line, whereas satellite 2 shows a nearly constant value of $\beta=2$. According to Creber *et al.* [18] satellite 1 must be

TABLE II. Binding energies, width and proposed assignment of the shakeup satellites of CH_4.

Satellite	Assignment	Energy rel. to C $(1s)^{-1}$, $v'=0$ (eV)			Width (eV)
See Fig. 5	Creber *et al.* [18]	Pireaux *et al.* [19]	Creber *et al.* [18]	This paper	This paper
1	$(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^1$	~15	15.66	16.6±0.3	6.5±1.0
2	$(1a_1)^{-1}(1t_2)^{-1}(3pt_2)^1$	19.2	18.91	19.2±0.1	1.0±0.1
3	$(1a_1)^{-1}(1t_2)^{-1}(4pt_2)^1$	22.7	22.01	22.7±0.3	1.5±0.5
4	$(1a_1)^{-1}(2a_1)^{-1}(3sa_1)^1$	26.5	26.89	26.3±0.2	5.0±1.0
5				30.6±0.2	1.5±0.5
6	$(1a_1)^{-1}(2a_1)^{-1}(4sa_1)^1$		34.84	32.5±0.5	7.0±1.5

dipole-forbidden, a conclusion which agrees with the observation of Pireaux *et al.* [19] that its intensity is pressure-dependent, suggesting an excitation by inelastic scattering processes. The present energy dependence suggests that the assignment of Creber *et al.* is correct and that the intensity of the feature in the near-threshold region derives from a conjugate shakeup process. The latter may be understood in terms of a dipole transition of the 1s electron to a bound state accompanied by the monopole excitation of a valence electron into the continuum. Such a process plays no role at high energies in the sudden limit, but near threshold the conjugate component of the transition moment becomes important, causing certain satellites to increase in intensity. In addition, new satellites which are forbidden in the sudden limit can appear at threshold, as is apparently observed in the present case. We note, however, that the β behavior of satellite 1 is unlike that observed for conjugate satellites in CO [5].

This latter result is important in that so far only three other molecules have been shown to exhibit conjugate shakeup behavior: CO [4,20–23], CO_2 [23], and N_2 [21–23]. Moreover, in methane it is possible to investigate conjugate shakeup behavior without the presence of a shape resonance, which normally has considerable influence on the partial cross section as well. The similarities in the Al $K\alpha$ shakeup spectra of methane, ethane (C_2H_6), and propane (C_3H_8) [19] may indicate that conjugate processes also play a role in the larger alkanes.

V. CONCLUSIONS

Angle-resolved photoelectron spectra of CH_4 have been measured with vibrational resolution between threshold and 385 eV photon energy. Partial cross sections and asymmetry parameters are given for the vibrationally excited ionic states $v'=0$, 1, and 2. From a Franck-Condon analysis in the high-energy region the equilibrium bond length in the core-excited ion was found to decrease by 0.047 Å to $R_e=1.039$ Å±0.001 Å compared to the neutral ground state. This contraction corresponds to a 9% increase in the $v'=1\leftarrow v''=0$ vibrational energy (396±2 meV compared to 361 meV). The $Z+1$ equivalent core model does not prove to be applicable.

The C $1s^{-1}$ core-hole lifetime broadening deduced from the PCI line shape visible in the photoelectron spectra is 83±10 meV which agrees well with theoretical predictions. Although comparison with the CO C $1s^{-1}$ lifetime shows the expected dependence of the Auger decay probability on the chemical environment of the core-hole state, the error bars are such that no definitive conclusions can be drawn on this point at present.

Although there is structure in the photoabsorption cross section at 303 eV photon energy, the lack of a shift in its energy in the different vibrational states of the ion suggests that a shape resonance is not involved. The structure appears to be due to doubly excited Rydberg states similar to those found in CO and N_2, a suggestion which is supported by recent Auger decay studies [44]. From the energies of the nearby shakeup satellite states as well as from the resonant Auger decay spectra of subthreshold Rydberg states the configuration of the states at ≈303 eV is thought to be either $(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^1(3pt_2)^1$ or $(1a_1)^{-1}(1t_2)^{-1}(3sa_1)^2$. This result has consequences for the location of the antibonding CH_4 $2t_2$ and $3a_1$ valence states in the photoabsorption spectrum: the experiment indicates that there is unlikely to be a shape resonance above threshold in CH_4 so that they presumably mix with the Rydberg states below threshold. Recent calculations do not agree on this point [14–17].

Six satellite lines were detected in the shakeup spectrum. The state of lowest energy relative to the main line shows a strong maximum in intensity just above threshold which suggests the occurrence of a conjugate shakeup process.

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