PHYSICAL REVIEW A **76**, 022509 (2007)

Probing the potential energy surface by high-resolution x-ray absorption spectroscopy: The umbrella motion of the core-excited CH_3 free radical

M. Alagia
ISMN-CNR, Sez. Roma1, P.le A. Moro 5, I-00185 Roma, Italy
and TASC-CNR, Area Science Park, Basovizza, I-34012 Trieste, Italy

M. Lavollée
LIXAM-CNRS, F-91898 Orsay-Cedex, France

R. Richter
Sincrotrone Trieste, Area Science Park, I-34012 Basovizza, Trieste, Italy

U. Ekström
Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden
and Institute of Chemical Physical Processes (CNR), Via Moruzzi 1, I-56124 Pisa, Italy

V. Carravetta
Institute of Chemical Physical Processes (CNR), Via Moruzzi 1, I-56124 Pisa, Italy

D. Stranges
Dipartimento di Chimica and INSTM, Universitá La Sapienza, P.le A. Moro 5, I-00185 Roma, Italy
and ISMN-CNR, Sez. Roma1, P.le A. Moro 5, I-00185 Roma, Italy

B. Brunetti
ISMN-CNR, Sez. Roma1, P.le A. Moro 5, I-00185 Roma, Italy

S. Stranges
Dipartimento di Chimica and INSTM, Universitá La Sapienza, P.le A. Moro 5, I-00185 Roma, Italy;
ISMN-CNR, Sez. Roma1, P.le A. Moro 5, I-00185 Roma, Italy;
and TASC-CNR, Area Science Park, Basovizza, I-34012 Trieste, Italy

(Received 10 January 2007; published 27 August 2007)

A detailed study of the umbrellalike vibration in inner-shell spectroscopy is presented. The high-resolution x-ray absorption spectrum for the lowest lying core excitation of the CH_3 free radical was recorded. High quality potential energy surfaces (PES) for the initial and final states of the transition were calculated as a function of the symmetrical stretching and the umbrella deformation coordinates. The strong anharmonicity along the umbrella coordinate in the double-well region of the PES of the core excited state has a strong effect on the bending vibrational progressions. The excellent agreement between the experiment and theory allows an accurate spectroscopic characterization of the vibrational structure of the electronic transition, and the estimation of the umbrella inversion time of 149 fs.

DOI: 10.1103/PhysRevA.76.022509 PACS number(s): 31.15.Ar, 33.55.Ad, 33.60.Cv, 82.80.Pv

I. INTRODUCTION

Recent developments in soft x-ray sources provide high resolution and intense light which gives new opportunities to study inner-shell excitation and ionization processes in free molecules [1,2]. The improved energy resolution allows investigation of previously inaccessible spectral fine structure [3–5]; however, detailed studies of vibrational structures in the x-ray absorption spectrum (XAS) of polyatomic molecules are still particularly difficult. Core excited states relax rapidly by Auger decay on the femtosecond scale. In special cases such as HBr [6], HCl [7], and others a repulsive potential energy surface is reached upon excitation of a core electron into a strongly antibonding virtual molecular orbital (MO). Then neutral dissociation can compete efficiently with electronic relaxation, affecting the decay dynamics. The short-lived nature of such highly excited states manifests itself in absorption features exhibiting large spectral broadening. This makes the vibrational structure difficult to resolve. For polyatomic molecules, which are characterized by multidimensional potential energy surfaces, the molecular shape (symmetry) may also change upon inner-shell excitation. The large number of vibrational modes that may be involved in the excitation process makes the study of the vibrational fine structure especially complex, both from an experimental and a theoretical point of view [8,9].

A particularly interesting case to study in polyatomic molecules is the planar↔nonplanar molecular deformation of AX_3 molecules caused by core-electron excitation at the central atom, which produces a symmetry lowering from the D_{3h} to the C_{3v} point group. The symmetrical out-of-plane bending mode in AX_3 systems is also called umbrellalike motion. Effects of this nuclear motion in spectra involving low energy excitations are well known and have been studied extensively. The NH_3 molecule is the simplest and most thoroughly investigated example in both the ir [10] and microwave spectroscopy [11]. The direct observation of such vibrational effects in inner-shell absorption spectroscopy is particularly difficult, since the bending vibrational structure is characterized by small energy spacing, and therefore masked effectively by the large core-hole lifetime broadening. Since no cases of detailed experimental characterization of umbrellalike motion in XAS have been published, the present study was aimed at investigating such process for a conveniently selected polyatomic molecule [12]. The lowest-lying core electron excitation in the CH_3 free radical was considered, namely, the process

$$(1a_1')^2(2a_1')^2(1e')^4 1a_2'' \rightarrow 1a_1'(2a_1')^2(1e')^4(1a_2'')^2, \quad (1)$$

where $1a_1'$ is the C 1s core orbital and $1a_2''$ the valence orbital, half-filled in the ground-state methyl radical.

II. THEORY

The theoretical description of the vibrational structure in the XAS of the CH_3 molecule due to process (1) was performed by first calculating the PES for the $^2A_2''$ ground state and the $^2A_1'$ core-excited state, and then considering the vibrational motion of the nuclei in these potentials. The molecular geometry of initial and final states of the transition is here given in terms of the HCH bond angle α_e and CH bond length r_e. The calculated values at equilibrium geometry are $\alpha_e=120°$ and $r_e=1.078$ Å for the $^2A_2''$ ground state, and $\alpha_e=114.7°$ and $r_e=1.016$ Å for the core excited $^2A_1'$ state. The CH bond length in the core excited molecule is shortened significantly and the planar symmetry (D_{3h}) deformed approaching the new pyramidal equilibrium geometry (C_{3v}). Although six vibrational modes are possible for the CH_3 molecule, only two of them, the symmetrical stretching and the symmetrical bending (umbrellalike mode), preserve the C_{3v} symmetry and allow the equilibrium geometry change. In the Born-Oppenheimer (BO) and Franck-Condon (FC) approximations, considering the symmetry of the initial (ground) and final electronic states, the only vibrational modes that are active, according to the selection rules, are the symmetric modes. The PES of the initial and final states of the transition were calculated as a function of the CH bond length and the bending angle θ measured as the deviation from the planar structure. The PESs were calculated using spin-restricted density functional theory with the Becke three-parameter Lee-Yang-Parr hybrid functional (B3LYP) [13] and the augmented correlation consistent polarized valence triple-zeta (aug-cc-pVTZ) [14] basis set, using the DALTON program [15]. The core excited state was explicitly optimized by imposing the 1s core hole as a condition on the Kohn-Sham wave function. This approach is well established for the core excited states [16]. The PES for the excited state exhibits a double-well structure, which is characterized by a very small inversion barrier of 45 meV. Adopting the BO approximation, the FC factors for the electronic excitation in Eq. (1) were calculated by separating the nuclear wave function Ψ into two parts, one containing the two C_{3v} symmetry preserving nuclear displacement coordinates q_1 and q_2, the other containing the rest of the system, $\Psi_{\text{vib}}(q_1,\ldots,q_6)=\Psi(q_1,q_2)\times\Psi'(q_3,\ldots,q_6)$. We are thus neglecting the coupling between these two sets of modes. Assuming the system to be initially in the vibrational ground state with respect to all normal modes—because the radical molecule is generated by adiabatic expansion in the supersonic jet—and that the C_{3v} symmetry of the system is preserved in the excitation, only the symmetric stretching and bending modes will be populated by the excitation event. The displacement vectors of the nuclear q_1 and q_2 coordinates were chosen as the normal mode vectors of the symmetric stretching and bending modes for the ground state. These two vectors span the space of C_{3v} symmetry preserving geometry distortions, and are preferred to the bond length and bending angle as coordinates for solving the vibrational problem, due to the simpler form of the kinetic energy term in the Hamiltonian in the q_1 and q_2 coordinates. The Schrödinger equation for the nuclear motion in the q_1 and q_2 coordinates was solved using the Hamiltonian $H=-\nabla_1^2/2m_1-\nabla_2^2/2m_2+V(q_1,q_2)$, where m_1 and m_2 are the effective masses of the displacement vectors, on a regular grid, using cubic interpolation for the potential. The FC factors were obtained by computing the overlap between ground-state and core-excited state vibrational wave functions.

III. EXPERIMENT

The experiments were carried out at the gas phase beamline of the storage ring Elettra [17] using the angle-resolved photoemission spectroscopy (ARPES) end station. The main vacuum chamber was equipped with a differentially pumped inner vessel to house a time-of-flight (TOF) 3D-ion-momentum-coincidence spectrometer [18]. The CH_3 radical was generated in a supersonic molecular beam by flash pyrolysis [19,20] of azomethane seeded in helium. An ion detector was also mounted close to the photon beam at about 30 cm from the skimmer-nozzle region, to record total-ion-yield (TIY) spectra of the thermalized radical in the expansion chamber, as well as spectra of CH_3/CH_4 gas mixtures for on line energy calibration. The photon flux for ion signal normalization was measured using a photodiode. The experimental XAS of the CH_3 molecule (TIY spectrum) was obtained using different conditions in various experiments.

IV. DISCUSSION

The high resolution TIY spectrum is shown in Fig. 1. The group of resonant features displayed in the figure is assigned to the vibrational structure of the lowest-lying core-excited state of $^2A_1'$ symmetry due to the transition in Eq. (1). As the transition is experimentally observed and theoretically calculated at approximately 6 eV below the next core-excited resonance [21], the vibrational structure of this transition does not overlap any other resonant feature in the spectrum. Figure 1 shows a dominant vibrational progression made of four components of decreasing intensity with large energy

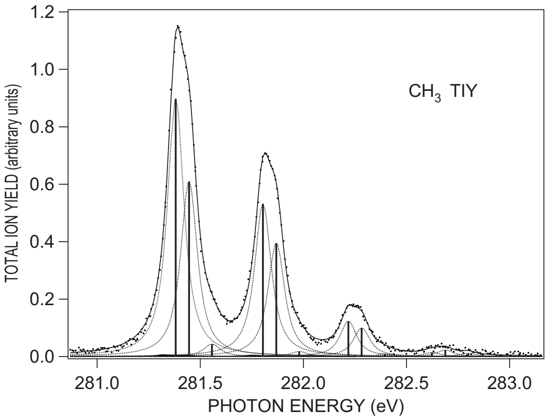

FIG. 1. The experimental high resolution XAS of CH$_3$. The best fit of the spectrum shows the twelve Voigt components (bars) describing the symmetrical stretching and bending vibrational progressions. The core-hole lifetime found as a free fit parameter is $\Gamma_L = 87 \pm 5$ meV.

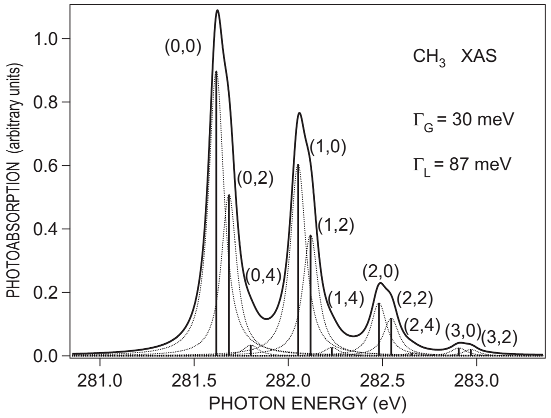

FIG. 2. The calculated XAS of CH$_3$. The theoretical relative intensities (FCFs) of the symmetrical stretching and bending vibrational progressions are convoluted using the experimental Γ_G and Γ_L parameters for comparison to the experimental XAS in Fig. 1.

separations. This progression is assigned to excitation of the symmetrical stretching mode $\nu_1(a_1')$. The vibrational components display an asymmetric profile with a tail on the high-energy side. Barely visible shoulders can be discerned on the high-energy flank of the two most intense components. This band structure can be ascribed to the convolution of an unresolved vibrational progression characterized by components with small energy separations. This is typical of bending progressions and it is therefore assigned to the excitation of the symmetrical bending mode $\nu_2(a_2)$, the umbrellalike motion. In this mode only the even vibrational states contribute to the spectrum, since all the odd states (with an odd value of the vibrational quantum number v) are symmetry forbidden. In this case, in fact, the FC factor would be vanishing because of the even symmetry of the ground-state vibrational wave function. The TIY spectrum is therefore analyzed in terms of twelve Voigt functions describing the vibronic states of the stretching and bending progressions. All functions are assumed to have the same Gaussian and Lorentzian widths, namely, the monochromator band pass used in the experiment $\Gamma_G = 30$ meV and the lifetime intrinsic broadening Γ_L used as a free fit parameter. The nonresonant residual ion signal is also taken into account in the best fit procedure as a free linear contribution. This background contribution has been subtracted from the spectrum shown in Fig. 1. The stretching progression in the fit is described by four Voigt functions located at excitation energies $E(0,0)$, $E(1,0)$, $E(2,0)$, and $E(3,0)$, while three Voigt functions only are considered for each bending progression and are located at energies $E(v_1,0)$, $E(v_1,2)$, $E(v_1,4)$, $v_1=0$, 1, 2, and 3 identifying the specific stretching band. The use of only three functions for each bending progression is suggested by the theoretical simulation of the absorption spectrum reported in Fig. 2. The four vibrational energy levels of the stretching progression, referred to the zero point energy, are described in the experimental data analysis by the usual formula $E_v - E_0 = \omega_e v - \omega_e x_e (v+1) v$, where ω_e, $\omega_e x_e$, and E_0 $[E(0,0)]$—the harmonic vibrational constant, the anharmonic coefficient, and the zero point energy—are free fit parameters, with higher order terms neglected. The same relationship is arbitrarily adopted in the fit of the bending progression (here $v=0,1,2$ corresponds to the three allowed even states), as a convenient general function containing two parameters, and thus suitable to describe the energy separations. The same parameters $\omega_e(\nu_2)$ and $\omega_e x_e(\nu_2)$ are used in the spectral analysis of all the four bending progressions, as suggested by the vibrational energy separations obtained theoretically. The best fit parameters obtained are 430.4 ± 1.4 meV and 3.5 ± 0.9 meV for $\omega_e(\nu_1)$ and $\omega_e x_e(\nu_1)$, and 17.8 ± 0.9 meV and -23.4 ± 0.4 meV for $\omega_e(\nu_2)$ and $\omega_e x_e(\nu_2)$, respectively. The chi-square fit procedure applied to the experimental TIY spectrum provides simultaneously the twelve experimental excitation energies [through the free fit parameters $E(0,0)$, $\omega_e(\nu_1)$ and $\omega_e x_e(\nu_1)$, $\omega_e(\nu_2)$ and $\omega_e x_e(\nu_2)$] and the twelve relative transition intensities, as the free fit amplitudes of the twelve Voigt functions.

Theoretical values for the same spectroscopic parameters have been extracted from the theoretical data by applying to the calculated excitation energy pattern the same formulas used to fit the experimental data. The results obtained for the stretching mode are 439.5 and 2.6 meV for $\omega_e(\nu_1)$ and $\omega_e x_e(\nu_1)$, respectively, while for the bending progressions the values 18.80 meV and −23.9 meV were derived for $\omega_e(\nu_2)$ and $\omega_e x_e(\nu_2)$, respectively.

The computed FC factors are reported in Fig. 2 as bars, located at the calculated transition energies, with labels (v_1, v_2) corresponding to the vibrational quantum numbers of the excited levels for the symmetrical stretching (v_1) and bending (v_2) modes. A Voigt function convolution with a Lorentzian component of 87 meV width (the natural linewidth found experimentally) and a 30 meV Gaussian was adopted to allow a comparison between the experimental spectrum (Fig. 1) and the theoretical results. The experimental parameters obtained by the analysis of several spectra together with the theoretical spectroscopic data are given in Table I.

Figures 1 and 2 and Table I show an overall excellent agreement between experiment and theory. The absolute excitation energies are in agreement within 0.27 eV, while the

TABLE I. Vibrational excitation energies E (meV) and relative intensities $I(v_1,v_2)$ for the lowest-lying core-excited state of CH_3. The experimental energies are referred to the adiabatic excitation energy $E(0,0)=281.35\pm0.04$ eV, as measured by calibration with CH_4. Theoretical energies and intensities (FCFs) are based on the calculated PES of initial and final states of the transition.

State	E_{exp}	I_{exp}	$I_{\mathrm{exp}}{}^{a}$	E_{theor}	I_{theor}	$I_{\mathrm{theor}}{}^{a}$
(0,0)	0	100	100	0	100	100
(0,2)	66±1	65±3		67	56.6	
(0,4)	178±2	5.5±0.5		183	3.8	
(1,0)	426±4	59±3	63±3	434	67.3	70
(1,2)	493±5	44±1		500	42.4	
(1,4)	605±6	4±1		613	2.9	
(2,0)	849±11	11±4	16±2	863	18.5	20
(2,2)	915±13	12±1		928	13.2	
(2,4)	1016±14	1.4±0.4		1039	0.9	
(3,0)	1266±23	2.0±0.8	3±1	1287	2.8	3
(3,2)	1332±24	1.7±0.9		1351	2.2	
(3,4)	1444±25	0.8±0.8		1459	0.2	

[a] Global band intensity.

relative vibrational separations (the energies are given in Table I) are predicted by the calculations within few percents (overestimated by 2.2–3.8 %). By applying a correction scale factor (3%) all the experimental energies are predicted by theory within 0.9%. The band profile change along the stretching progression in the TIY is also well reproduced in the calculated XAS. However, a small discrepancy is observed for the relative band intensities. This may be due, at least in part, to a possible change in the ionization efficiency among the different vibrational-excited resonance states after photoabsorption.

The very low inversion barrier of the core-excited CH_3, 45 meV, makes a theoretical treatment beyond the harmonic approximation necessary. The applicability of DFT to systems with a core hole, a special kind of excited state from the point of view of density functional theory (DFT), is shown by the excellent agreement between theory and experiment. The method used gives very high quality results because anharmonicities of the potential energy surfaces are taken fully into account. However, as here implemented, it is restricted to two coupled vibrational degrees of freedom.

The high accuracy of the calculations suggests that the theoretical energy separation $E(0,1)-E(0,0)=13.8$ meV can be used for estimating the umbrella inversion time of the lowest-lying vibronic state of the core-excited CH_3. The time τ necessary for the molecule to invert from one pyramidal form to the other is given by the formula $\tau=h(2\Delta E)^{-1}$, where ΔE is the energy splitting, which in our case is 13.8 meV. The inversion time thus calculated is 149 fs, which can be compared with the core-hole lifetime measured experimentally as approximately 8 fs ($\Gamma_L=87$ meV).

V. CONCLUSIONS

Effects of the umbrellalike vibration were studied in detail by inner-shell spectroscopy on a very low density target of CH_3. The high resolution XAS was recorded by combining an efficient supersonic jet source to generate the CH_3 radical with an intense and high resolution synchrotron radiation source. The rich vibrational structure observed in the spectrum was analyzed in terms of the excitation of the symmetrical stretching and the symmetrical out-of-plane bending (umbrella mode), accompanying the core electron excitation. The strong anharmonicity of the PES of the excited state along the bending coordinate, due to the small potential barrier, has a profound effect on the energy and relative intensity patterns of the bending vibrational progression. A detailed characterization of the double-well potential energy surface of the excited state and the determination of spectroscopic parameters of the transition were achieved by accurate theoretical calculations. Excellent agreement between experimental and simulated x-ray absorption spectra was observed and from the very small potential barrier computed a consequently short umbrella inversion time (≈149 fs) was predicted. A contribution of other vibrational modes to the spectrum cannot be excluded, but the agreement between the experiment and theory indicates that the two symmetrical modes that allow the molecule to move from the planar to the pyramidal equilibrium geometry are dominant. Extending the study of CH_3 to the isotopomer CD_3 can improve our understanding of the XAS vibrational structure, and further verify the accuracy of the theoretical-experimental approach used in this work. Such an investigation is presently in progress.

ACKNOWLEDGMENTS

This work was supported by the Italian MUR and CNR.

---

[1] K. Ueda, J. Phys. B **36**, R1 (2003).
[2] U. Hergenhahn, J. Phys. B **37**, R89 (2004).
[3] H. Yoshida, K. Nobusada, K. Okada, S. Tanimoto, N. Saito, A. De Fanis, and K. Ueda, Phys. Rev. Lett. **88**, 083001 (2002).
[4] Y. Muramatsu, K. Ueda, N. Saito, H. Chiba, M. Lavollée, A. Czasch, T. Weber, O. Jagutzki, H. Schmidt-Böcking, R. Moshammer, U. Becker, K. Kubozuka, and I. Koyano, Phys. Rev. Lett. **88**, 133002 (2002).
[5] S. Stranges, R. Richter, and M. Alagia, J. Chem. Phys. **116**, 3676 (2002).
[6] P. Morin and I. Nenner, Phys. Rev. Lett. **56**, 1913 (1986).
[7] O. Björneholm, S. Sundin, S. Svensson, R. R. T. Marinho, A. Naves de Brito, F. Gel'mukhanov, and H. Ågren, Phys. Rev. Lett. **79**, 3150 (1997), and references therein.
[8] D. Hübner, F. Holch, M. L. M. Rocco, K. Prince, S. Stranges, A. Schöll, E. Umbach, and R. Fink, Chem. Phys. Lett. **415**, 188 (2005).
[9] G. Contini, V. Carravetta, P. Parent, C. Laffon, and G. Pol-

zonetti, Surf. Sci. **457**, 109 (2000).

[10] G. Herzberg, *Molecular Spectra and Molecular Structure* (Krieger, Florida, 1991), Vol. 2, p. 294, and references therein.

[11] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), p. 300, and references therein.

[12] The choice of the transition and the molecule investigated in this work is discussed in a forthcoming paper along with a detailed description of the experimental and theoretical methods, and the results of a comparative study which involves the CD_3 molecule.

[13] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[14] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[15] DALTON, a molecular electronic structure program, release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html

[16] L. Triguero, O. Plashkevych, L. G. M. Pettersson, and H. Agren, J. Electron Spectrosc. Relat. Phenom. **104**, 195 (1999), and references therein.

[17] R. R. Blyth, R. Delaunay, M. Zitnik, J. Krempasky, R. Krempaska, J. Slezak, K. C. Prince, R. Richter, M. Vondracek, R. Camilloni, L. Avaldi, M. Coreno, G. Stefani, C. Furlani, M. de Simone, S. Stranges, and M. Y. Adam, J. Electron Spectrosc. Relat. Phenom. **101-103**, 959 (1999).

[18] M. Lavollée, Rev. Sci. Instrum. **70**, 2968 (1999).

[19] D. W. Kohn, H. Clauberg, and P. Chen, Rev. Sci. Instrum. **63**, 4003 (1992).

[20] D. Stranges, M. Stemmler, X. Yang, J. D. Chesko, A. G. Suits, and Y. T. Lee, J. Chem. Phys. **109**, 5372 (1998).

[21] U. Ekström, V. Carravetta, M. Alagia, M. Lavollée, R. Richter, C. Bolcato, and S. Stranges (unpublished).