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Vibrational effects in the photo-ion yield spectrum of the SiH_2^+ molecular ion following 2p inner-shell excitation

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Abstract. We report on complementary theoretical and laboratory investigations of the 2p ion yield cross sections for the molecular-ion series SiH_n^+ (n = 1, 2, 3), in the 95-108 eV photon energy range, below the L-shell threshold. The experiments used an electron cyclotron resonance (ECR) plasma molecular-ion source coupled with monochromatised synchrotron radiation in a merged-beam configuration. The experimental spectra are compared with total photoabsorption cross-sectional profiles calculated using an ab initio configuration interaction method inclusive of spin-orbit coupling and the vibrational dynamics. The experimental results show vibrationally resolved resonances for SiH_2^+ in the 98-102 eV range. The calculations indicate twenty four core-excited states below the energy of 102 eV, of which only four contribute significantly to the observed spectrum. These states correspond to the excitation of an atomic-like 2p electron to the SiH_2^+ ($5a_1$) valence orbital.

1. Introduction

The experimental study of the interaction of short wavelength photons with atomic ions has become a mature field of research, due largely to the use of dedicated ion sources coupled with high-resolution photon beam lines at 3rd generation synchrotron radiation facilities worldwide. Utilising the photon-ion, merged-beam technique, synchrotron-based experiments provide high quality data, including target ion selectivity, discrimination between different ion production channels, high spectral resolving power and the possibility of absolute cross section measurements. The wide range of atomic ion species studied to date through the photon-ion merged beam technique has been covered in comprehensive reviews [1-3].

Molecular ions also play key roles in many astrophysical environments, processing plasma applications, energy storage and combustion chemical processes, where joint radiative processes are also important [4 and references therein]. Yet, systematic studies on the core-shell photoionisation of

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molecular ions are still in the relatively early stages with only a small number of results to date [5, 6 and references therein].

This relative paucity of knowledge on molecular ions photoionisation is largely due to associated additional experimental and theoretical challenges. In a molecular ion, the electronic relaxation (Auger) processes of a core-hole created by the photo-excitation of an inner-shell electron localised on an atomic site can be affected by the related changes in the reduced valence electrons distribution and its coupling to the nuclear motion degrees of freedom, leading to nuclear relaxation (dissociation) processes. For shallow core-levels (soft x-ray region) in molecules, the typical core-hole lifetimes and vibrational characteristic times are comparable, of the order of a few fs or more. The nuclear dynamics interactions may be revealed in the form of significant broadening effects in the photoabsorption spectrum near threshold or show up as specific features in the spectra of the products of the core-hole decay (Auger electrons, x-ray fluorescence photons and photo-ions) [7]. The study of electron-nuclear motion interactions in molecular ions remains largely unexplored and the present work constitutes a first step towards systematic studies.

The paper focuses on silicon hydride molecular ions, which are of significant interest in astrophysical and technologically important plasma sources [4]. In particular, we focus on new results showing vibrationally resolved inner-shell resonances in the photo-ion cross-section of SiH_2^+. Ab initio electronic structure and dynamics calculations support the interpretation of the results.

2. Experimental details

The experiments were performed on the PLEIADES beam line at the SOLEIL synchrotron facility. The hydride ions were produced in an electron cyclotron resonance ion source (ECRIS) by heating silane (SiH_4) gas with a 12.6 GHz microwave source. After extraction, charge to mass separation of the ions was performed using a dipole magnet arrangement and the selected ions were merged with the synchrotron photon beam in a 0.6m overlap interaction region. An electrostatic lens at the end of the interaction region refocused the dissociated fragments. A combination of a dipole magnet and electrostatic velocity sector enabled charge to mass separation of the produced charged fragments. The latter were counted using a microchannel plate detector, while the transmitted (un-dissociated) ions were collected in a Faraday cup. A fuller description of the experimental arrangements and data analysis techniques is provided in [4].

We point out that, due to the angular distribution of the fragments released by dissociation of core-excited molecular target ions, the higher charged ions produced by the synchrotron photons may not be collected efficiently. We mitigate this problem by investigating hydride ions, as the present case of SiH_n^+ involves a large difference in mass between the hydrogen atom and the silicon, so that following molecular dissociation the silicon ions remain fairly well on their original track. The lighter fragments such as H^+ or H_2^+ are much less likely to fall within the collection solid angle for detection and are thus not easily detected. Si^{2+} ions, however, remain detectable with good efficiency.

3. Theoretical details

Details on the calculations of the potential energy surfaces (PES) and dipole moments are given in [4]. In brief, they were computed using the Configuration Interaction Single (CIS) method. The spin-orbit coupling was taken into account through the full Breit-Pauli operator. A aug-cc-pvQz basis set was used and 7s, 6p, 5d, 3f diffuse functions were added on Si. All electronic structure calculations were performed with the GAMESS-US package [8]. Furthermore, we employed the harmonic approximation in normal coordinates for the PES of all electronic states. The vibrational wavefunctions, and thus the Franck-Condon factors, were computed on a spatial grid defined along each normal coordinate within the sine-discrete variable representation (sine-DVR) [9]. The absorption spectra were computed using a standard wave packet method [10]. For each core-excited electronic state the initial nuclear wavefunction multiplied by the dipole transition moment was propagated on the corresponding PES. The autocorrelation function was thus obtained. The absorption spectrum was then determined by Fourier transform of the autocorrelation function.

4. Results and Analyses

4.1. The SiH^+, SiH_2^+, SiH_3^+ series

We have recently reported a comparison of experimental and theoretical results for inner-shell photoionisation of the SiH_n^+ (n = 0 - 3) sequence in the 105-120 eV range [4], with detection in the Si^{2+} channel. Figure 1 shows the overview of the measured cross sections in the L-shell excitation region as the number of bonded neutral hydrogens is changed. The evolution of the spectra, in the 105 to 120 eV photon energy range, is clearly evidenced as a shift towards lower energies as the number of bonded hydrogen atoms increases. For all three hydride species, the spectra (red, green, blue) in the 105-120 eV energy were interpreted by extensive ab initio calculations in terms of 2p core electron excitations in both ground and metastable initial states [4]. Each spectrum divides into three characteristic photon energy regions. (1) Sharp core to Rydberg series above ~ 112 eV. The more atomic-like resonance profiles indicate weaker vibrational effects in this region. (2) A strong core to valence excitation region between ~ 109 eV (SiH_3^+) and ~ 111 eV (SiH^+, SiH_2^+) where no vibrational structure is observable due to the large spectral overlap between many broadened electronic transitions very close in energy. (3) A broad and shallow region between ~ 104-107 eV corresponding to 2p excitation to an anti-bonding valence molecular orbital. The latter leads to repulsive states and the molecule dissociates directly on a very short time scale. The resonance appears featureless and considerably broadened due to the wide Franck-Condon envelope.

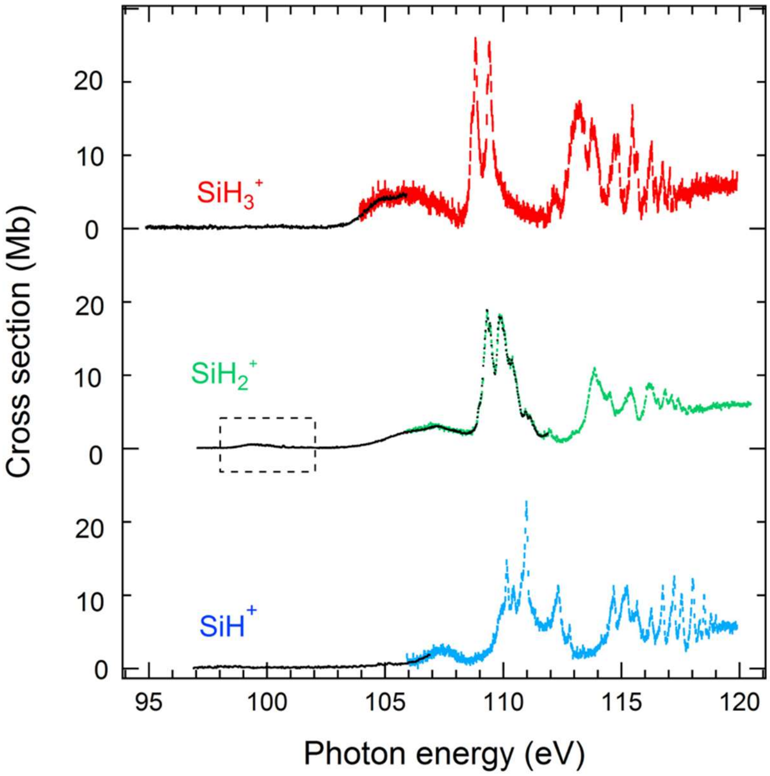

Figure 1. Total photo-absorption cross-section of the SiH^+, SiH_2^+, SiH_3^+ molecular hydride ions measured using photo-ion yield spectroscopy with synchrotron radiation in the L-shell threshold photon region. The 98-102 eV region is of particular interest for SiH_2^+ as it includes vibrationally resolved electronic transitions.

The theoretical investigations predicted additional structures at photon energies lower than 105 eV. This motivated a subsequent beam time investigation. The new experimental results are shown in black in Figure 1 as an extension to lower photon energies and join on smoothly to the data for the 105 -120 eV region. There are observable structures for the SiH_2^+ case in the 98-102 eV range (see area marked by the rectangle) showing quite well resolved lines which are interpretable as the vibrational structure of ground to core-excited electronic transitions.

4.2. The SiH_2^+ spectrum in the 98 - 102 eV photon energy region

The SiH_2^+ scan of Figure 1 was examined with better experimental statistics and resolution than for the SiH^+ and SiH_3^+ cases where no analogous structures were observed. The detailed experimental spectrum obtained at a spectral resolution of 35 meV, the overall theoretical prediction and the assignment of the vibrational resonances to the main contributing core-excited molecular states are shown in Figures 2(a), (b) and (c), respectively. The cross section values in the 98-102 eV energy region are below 1 Mbarn. Table 1 provides the energies and integrated areas of the experimental peaks, numbered according to Figure 2(a). The experimental spectrum exhibits a series of peaks (labelled 4 -18) separated by a roughly constant energy interval of about 0.13 eV. The peak energies and integrated areas in Table 1 were obtained from the underlying least square fitted Gaussian profiles shown in Fig 2a. In obtaining the Gaussian fits the data were divided into three sets (peaks 1-3, 4-9 and 10-18). The Gaussian profiles were determined, using the same line width and spacing within each set, with the optimum values obtained from a least square fitting procedure.

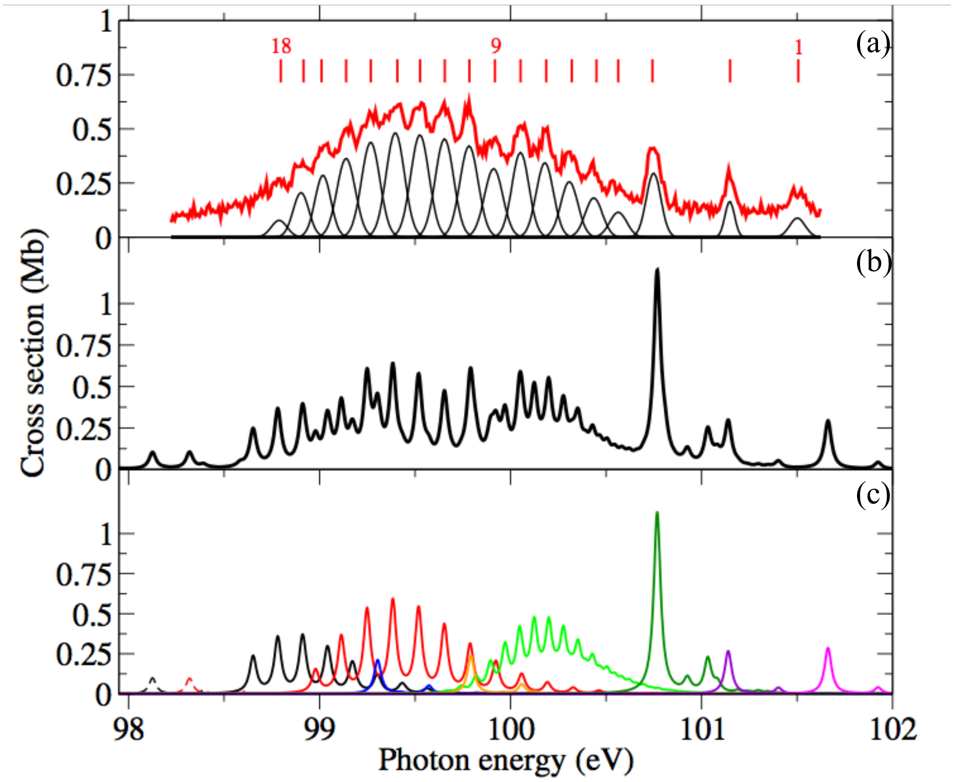

Figure 2. Experimental and theoretical total photoabsorption cross section spectra of the SiH_2^+ molecular ion in the 98-102 eV region: (a) experimental spectrum, (b) ab-initio total cross section including vibrational dynamics and (c) details showing the electronic core states which contribute mostly to the cross section in this region (see text for details).

Table 1. Parameters of vibrationally resolved peak positions in the experimental 2p inner-shell excitation spectrum of the SiH_2^+ molecular ion. The peak numbers are shown in Figure 2(a).

Peak number	Peak photon energy (eV)	Peak area (Mb eV)
18	98.788	0.008
17	98.903	0.021
16	99.018	0.030
15	99.139	0.044
14	99.268	0.053
13	99.396	0.058
12	99.525	0.057
11	99.654	0.055
10	99.783	0.051
9	99.911	0.038
8	100.052	0.044
7	100.180	0.039
6	100.308	0.029
5	100.435	0.020
4	100.563	0.013
3	100.749	0.028
2	101.147	0.010
1	101.502	0.009

SiH_2^+ belongs to the C_{2v} symmetry point group with normal vibrational modes Q_0 (asymmetric stretching), Q_1 (symmetric stretching) and Q_2 (bending). SiH_2^+ has doublet spin multiplicity and $(1a_1)^2$ $(2a_1)^2$ $(1b_1)^2$ $(1b_2)^2$ $(3a_1)^2$ $(4a_1)^2$ $(2b_1)^2$ $(5a_1)^1$ configuration in the ground state (GS). The results of the calculations show bound potential energy curves correlating to the $[Si(2p^{-1})H]^+ + H(1s)$ dissociation limits, at energies less than 102 eV above the GS. These core-excited states support the vibrational levels involved in the observed structure. The calculations indicate twenty four core-excited electronic states, corresponding to the excitation of a Si 2p electron to the $(5a_1)$ valence molecular orbital, below the energy of 102 eV. All their contributions were integrated to compare with the experimental results. However, four of these doubly-degenerate spin-orbit split core-excited states contribute most significantly to the spectrum as shown in Figure 2(c). The vertical energies, oscillator strengths, normal mode frequencies and Franck-Condon factors for these states are given in Table 2.

The states numbering, e.g. 13-14, in the first column of Table 2 is for accounting purposes only and the adjacent number pairings indicate the aforementioned associated degeneracies. The black, red, light green and dark green coloured traces of Figure 2(c) correspond to the 13-14, 15-16, 19-20 and 23-24 core-excited electronic states, respectively. Using a single global energy shift of + 0.7 eV, the relative positions of the experimental peaks in Figure 2(a) are quite well reproduced by the theoretical spectrum shown in Figure 2(b) and confirm that the observed fine structure of Figure 2(a) is due to the vibrational nuclear dynamics of the molecule while in certain low-lying bound core-excited electronic states. This result implies that the lifetimes of the core-excited states must be sufficiently long to allow vibrational motion to establish. The absolute values of the cross sections are also generally in good agreement between experiment and theory, although Figure 2 suggests that the oscillator strengths corresponding to the states 23-24 are somewhat overestimated in our calculations. The results of the vibrational dynamics calculations show that for states 13-14, 15-16 and 19-20 the vibrational progression is due predominantly to the bending mode (Q_2). For states 23-24, the asymmetric stretching (Q_0) and bending modes (Q_2) are populated after core-excitation.

Table 2. Theoretical electronic energy, oscillator strength and vibrational parameters of the main 2p inner-shell resonances of SiH_2^+ in the 98-102 eV photon energy region.

Electronic state	Vertical energy (eV)	Oscillator strength	Normal mode[c] frequency (cm^{-1})	Franck-Condon factors[d,e]				
GS[a]	0.00	-	Q_0 2318					
			Q_1 2236					
			Q_2 918					
13-14[b]	98.06	0.0062	Q_0 2164	0.80 (0)	0.18 (1)			
			Q_1 2222	1.00 (0)				
			Q_2 1041	0.17 (0)	0.26 (1)	0.23 (2)	0.16 (3)	
15-16[b]	98.37	0.012	Q_0 2187	0.84 (0)	0.14 (1)			
			Q_1 2243	1.00 (0)				
			Q_2 1086	0.13 (1)	0.18 (2)	0.19 (3)	0.16 (4)	0.12 (5)
19-20[b]	98.94	0.0119	Q_0 2166	0.82 (0)	0.17 (1)			
			Q_1 2222	1.00 (0)				
			Q_2 616	0.10 (6)	0.13 (7)	0.15 (8)	0.15 (9)	0.12 (10)
23-24[b]	99.51	0.0057	Q_0 2134	0.83 (0)	0.16 (1)			
			Q_1 2186	1.00 (0)				
			Q_2 1273	0.88 (0)				

[a] All the transitions originate from the ground state (GS) of SiH_2^+ assumed to be in zero vibrational level.
[b] These numbers are for labelling purposes only (see text of paper for details).
[c] Q_0 (asymmetric stretching), Q_1 (symmetric stretching) and Q_2 (bending).
[d] Only values greater than 0.1 are given.
[e] The number in brackets is the vibrational number in the core excited state.

5. Conclusions

We have extended experimental and theoretical studies of inner-shell excitation of the SiH_n^+ molecular ion series to lower photon energies and unveiled vibrationally resolved resonances in the case of SiH_2^+. The experimental results are satisfactorily explained in terms of a small number of spin orbit split states, for which the energy predictions, oscillator strengths and normal mode frequencies are presented.

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