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Supplementary Information – Single-photon ionization of SiC in the gas phase: experimental and *ab initio* characterizations of SiC^+

B. Gans,*[a] J. Liévin,[b] P. Halvick,[c] N. L. Chen,[a] S. Boyé-Péronne,[a] S. Hartweg,[d]‡ G.A. Garcia,[d] and J.C. Loison[c]

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1 Effect of the core and core-valence correlation and of the basis set on the $1^+\,^2\Pi$ electronic state potential energy curve

In this section, we discuss the $1^+\,^2\Pi$ double well shape, when going from *V*/AV5Z to *CV*/ACV6Z calculations. As shown in the left panel of Figure S1, the lowest minimum moves from the larger internuclear distance (1.94 Å) to the smaller one (1.74 Å). As a consequence the lowest vibrational levels are shifted to lower energies and the maximum vibrational overlaps occur at shorter distances, *i.e.* closer to the minima of the X and a states of SiC. The result of these changes on the calculated photoelectron spectra is illustrated in the right panels of Figure S1. Apart from a slight red shift of about 40 meV of both transitions, this does not change our conclusion described in the main paper concerning a "matching" with the experimental photoelectron spectrum for the $1^+\,^2\Pi \leftarrow X\,^3\Pi$ transition, and an "unmatching" for the $1^+\,^2\Pi \leftarrow a\,^1\Sigma^+$ transition.

2 Procedure used for estimating the photoionization probabilities

Table S1 gives, for the different states of SiC and SiC^+, the weights *w* of the main configurations involved in single electron ionization processes. These weights correspond to the squares of the CI coefficients of the considered configurations in the MRCI/AV5Z wave functions obtained at $R = 1.72$ Å, close to the

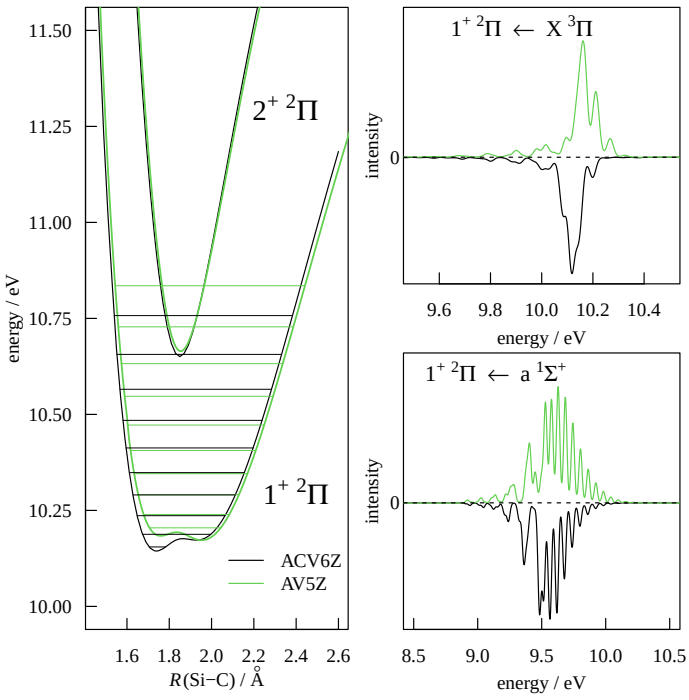

Fig. S1 On the left side, potential energy curves of the first two $^2\Pi$ states of SiC^+ computed at the MRCI+Q/AV5Z (in green) and MRCI+Q/ACV6Z (in black) levels of theory. On the right side, corresponding calculated photoelectron spectra for the $1^+\,^2\Pi \leftarrow X\,^3\Pi$ and $1^+\,^2\Pi \leftarrow a\,^1\Sigma^+$ transitions using the same color code.

* *Corresponding author: berenger.gans@universite-paris-saclay.fr*
[a] *Institut des Sciences Moléculaires d'Orsay, CNRS, Université Paris-Saclay, F-91405 Orsay, France*
[b] *Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing, Université Libre de Bruxelles, CP 160/09, B-1050 Bruxelles, Belgium*
[c] *Institut des Sciences Moléculaires, CNRS, Université de Bordeaux, F-33400 Talence, France*
[d] *Synchrotron SOLEIL, L'Orme des Merisiers, St. Aubin, F-91192 Gif sur Yvette, France*
‡ *current address: Institute of Physics, University of Freiburg, 79104 Freiburg, Germany*

ground state geometry of SiC. Let us note that in the case of the $2^+\,^2\Pi$ state, the main configuration with w= 0.77 does not obey the single electron ejection condition, and does not therefore contribute to the photoionization. The secondary configuration obeys the condition, but with a negligeable weight.

The probabilities P of the photoionizing transitions are provided in Table S2. They are given by the formula: $P = w_\mathrm{n} \cdot w_\mathrm{c} \cdot g_\mathrm{n} \cdot g_\mathrm{c}$, where w_n and w_c are the weights for the neutral and the cation, respectively, and g_n and g_c are the corresponding degeneracies, including the orbital and spin contributions. $P_\mathrm{norm.}$ are the probabilities normalized with respect to the main $\mathrm{X}^+\,^4\Sigma^- \leftarrow \mathrm{X}\,^3\Pi$ photoionizing transition.

Table S1 Main configurations and their corresponding weights (w) for the different states of SiC and SiC^+ involved in photoionizing transitions implying single electron ejection.

State	w	Main configuration
$\mathrm{X}\,^3\Pi$	0.77	$[...]7\sigma^1 2\pi^3$
$\mathrm{a}\,^1\Sigma^+$	0.71	$[...]7\sigma^0 2\pi^4$
$\mathrm{X}^+\,^4\Sigma^-$	0.87	$[...]7\sigma^1 2\pi^2$
$1^+\,^2\Delta$	0.85	$[...]7\sigma^1 2\pi^2$
$1^+\,^2\Pi$	0.71	$[...]7\sigma^0 2\pi^3$
$1^+\,^2\Sigma^-$	0.86	$[...]7\sigma^1 2\pi^2$
$1^+\,^2\Sigma^+$	0.82	$[...]7\sigma^1 2\pi^2$
$2^+\,^2\Pi$	0.77*	$[...]7\sigma^2 2\pi^{1}*$
	0.04	$[...]7\sigma^0 2\pi^3$

* The main configuration does not lead to ionization (see text).

Table S2 Pertinent parameters for the photoionization probabilities of each photoionizing transitions used in the calculated photoelectron spectrum of Fig. 5 of the main paper.

Transitions	w_n	w_c	g_n	g_c	P	$P_{norm.}$*
$X^{+\,4}\Sigma^- \leftarrow X^3\Pi$	0.77	0.87	6	4	16.2	1.0
$1^{+\,2}\Delta \leftarrow X^3\Pi$	0.77	0.85	6	4	15.8	1.0
$1^{+\,2}\Pi \leftarrow X^3\Pi$	0.77	0.71	6	4	13.2	0.8
$1^{+\,2}\Sigma^- \leftarrow X^3\Pi$	0.77	0.86	6	2	8.0	0.5
$1^{+\,2}\Sigma^+ \leftarrow X^3\Pi$	0.77	0.82	6	2	7.6	0.5
$2^{+\,2}\Pi \leftarrow X^3\Pi$	0.77	0.04	6	4	0.8	0.0
$1^{+\,2}\Pi \leftarrow a^1\Sigma^+$	0.71	0.71	1	4	2.0	0.1

* Normalized probability.