To see $\text{C}_2$: Single-photon ionization of the dicarbon molecule

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ABSTRACT

The C\textsubscript{2} carbon cluster is found in a large variety of environments including flames, electric discharges, and astrophysical media. Due to spin-selection rules, assessing a complete overview of the dense vibronic landscape of the C\textsubscript{2}\textsuperscript{+} cation starting from the ground electronic state \(X^+ 4\Sigma_g^+\) of the neutral is not possible, especially since the C\textsubscript{2} ground state is of \(X^+ 4\Sigma_g^+\) symmetry. In this work, a flow-tube reactor source is employed to generate the neutral C\textsubscript{2} in a mixture of both the lowest singlet \(X^+ 1\Sigma_g^+\) and triplet \(a^3\Pi_a\) electronic states. We have investigated the vibronic transitions in the vicinity of the first adiabatic ionization potential via one-photon ionization with vacuum ultraviolet synchrotron radiation coupled with electron/ion double imaging techniques. Using \textit{ab initio} calculations and Franck-Condon simulations, three electronic transitions are identified and their adiabatic ionization energy is determined \(E_i(a^3\Pi_a \leftrightarrow X^+ 1\Sigma_g^+) = 12.440(10)\) eV, \(E_i(X^+ 4\Sigma_g^+ \leftrightarrow a^3\Pi_a) = 11.795(10)\) eV, and \(E_i(a^3\Pi_a \leftrightarrow a^3\Pi_a) = 12.361(10)\) eV. From the three origin bands, the following energy differences are extracted: \(\Delta E(a \rightarrow X) = 0.079(10)\) eV and \(\Delta E(a^3 \rightarrow X^+) = 0.567(10)\) eV. The adiabatic ionization potential corresponding to the forbidden one-photon transition \(X^+ \leftrightarrow X\) is derived and amounts to 11.873(10) eV, in very good agreement with the most recent measurement by Krechkivska \textit{et al.} \cite{Krechkivska2016}. The enthalpy of formation of the doublet ground state C\textsubscript{2} ions cation in the gas phase is determined at 0 K, \(\Delta h^i(0K)(C_2(3\Pi_g^+)) = 209.9(10)\) kJ mol\(^{-1}\). In addition, we report the first experimental ion yield of C\textsubscript{2} for which only a simple estimate was used up to now in the photochemistry models of astrophysical media due to the lack of experimental data.

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The dicarbon molecule (C\textsubscript{2}) is ubiquitous in many environments such as flames, plasmas, and astrophysical media, being the first transient species to have been identified in the coma of a comet. The omnipresence of C\textsubscript{2} in diffuse interstellar clouds allowed some Diffuse Interstellar Bands to be named C\textsubscript{2}-DIBs because they are detected in interstellar clouds that are characterized by high column densities of C\textsubscript{2} molecules. Given the intense UV radiation in these environments, the quantification of C\textsubscript{2} photoionization is important as this constitutes a source of C\textsubscript{2}\textsuperscript{+}, which is a much more reactive species than C\textsubscript{2} which only reacts slowly with H\textsubscript{2}. Although the absorption and emission spectroscopies of this species and its cation have been extensively studied theoretically and experimentally, photoionization studies were mainly limited to theoretical works. Only recently, Krechkivska \textit{et al.} reported for the first time a measurement of its adiabatic ionization potential (IP) \((X^+ 4\Sigma_g^+ \leftrightarrow X^+ 1\Sigma_g^+)\) using resonant two-photon threshold-ionization spectroscopy. In their work, they produced C\textsubscript{2} in its a^3\Pi_a metastable state using an electric discharge and ionized it toward its cationic ground state through the neutral 4^3\Pi_g electronic state. To our knowledge, no single-photon ionization experiment has been performed up to now. The ground electronic states of C\textsubscript{2} and C\textsubscript{2}\textsuperscript{+} being \(X^+ 1\Sigma_g^+\) and \(X^+ 4\Sigma_g^+\), a single-photon
ionizing transition between these two states is spin-forbidden. Thus, C$_2$ must be photoionized from the a$^2$I$_{u}$ metastable state to reach the cation ground state. In order to have a complete overview of the photoionization of C$_2$, it is necessary to use broadly tunable vacuum ultraviolet (VUV) radiation coupled to a sensitive mass-selective photoelectron spectrometer, C$_2$ being generally produced in a complex mixture containing several species and in small quantities.

In this paper, we report the first single-photon ionization of C$_2$ in the vicinity of the adiabatic ionization potential (IP). The experiments were performed at the DESIRS beamline$^{15}$ of the French SOLEIL synchrotron facility. All of the experimental details have been described previously.$^{11,15}$ F atoms, produced by a microwave discharge applied to F$_2$, and CH$_4$ diluted in He were introduced in the flow-tube reactor. The experimental conditions (gas flow and relative concentrations) were optimized in order to produce C$_2$ by secondary reactions. In these conditions, several species were generated (CH$_x$, C$_2$H$_y$, C$_3$H$_z$, ... with $x = 0, 1, 2, ...$). Due to the exothermicity of consecutive H abstraction and secondary reactions, the products can be formed with high vibrational temperature and in excited metastable states. The resulting gas flow is then skimmed twice before crossing at right angle the monochromatized synchrotron radiation in the double-imaging photoelectron/photoion spectrometer DELICIOUS III. The photon resolution in the range of 11.5–14 eV was $\delta E = 9$ meV. The spectrum was corrected for photon flux fluctuations using the photodiode (AXUV100, IRD) current recorded over the scan range. The photoelectrons were extracted by an 88 V/cm field, and the offline analysis of their corresponding mass-selected velocity map images was set to provide a total resolution, including the photon energy contribution, of approximately 25 meV on the threshold photoelectron (TPE) spectrum, which was obtained applying the slow photoelectron (SPE) method described previously.$^{13}$ The absolute calibration of the energy scale was performed using argon lines (present in the gas filter of the

![FIG. 1. Calculated potential energy surfaces of C$_2$ and C$_2^+$ as a function of the d(C–C) distance.](image_url)

**TABLE I.** C$_2$ and C$_2^+$ electronic state energies extrapolated to the CBS limit (see text).

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>Main configurations</th>
<th>$E$ (CBS) (hartree)</th>
<th>$E_{\text{Lamb}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$</td>
<td>X$^1\Sigma_g^+$</td>
<td>71% (2$\sigma_u$)$_2$(1$\pi_u$)$_1^3$ + 14% (2$\sigma_u$)$_6$(1$\pi_u$)$_4$(3$\sigma_g$)$_2^2$</td>
<td>−75.811 535</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>a$^3\Pi_u$</td>
<td>88% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\pi_g$)$_1^3$ + 5% (2$\sigma_u$)$_4$(1$\pi_u$)$_2$(3$\sigma_g$)$_2$(1$\pi_g$)$_1$</td>
<td>−75.809 599</td>
<td>0.053</td>
</tr>
<tr>
<td>C$_2^+$</td>
<td>X$^4\Sigma_g^-$</td>
<td>86% (2$\sigma_u$)$_2$(1$\pi_u$)$_2$(3$\pi_g$)$_1^3$ + 7% (2$\sigma_u$)$_6$(1$\pi_u$)$_4$(3$\sigma_g$)$_2$(1$\pi_g$)$_1$</td>
<td>−75.377 781</td>
<td>11.803</td>
</tr>
<tr>
<td></td>
<td>a$^2\Pi_u$</td>
<td>72% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\pi_g$)$_1^3$ + 13% (2$\sigma_u$)$_6$(1$\pi_u$)$_4$(3$\sigma_g$)$_2$(1$\pi_g$)$_1$</td>
<td>−75.356 565</td>
<td>12.381</td>
</tr>
<tr>
<td></td>
<td>A$^4\Pi_g$</td>
<td>86% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\pi_g$)$_1^3$ + 6% (2$\sigma_u$)$_4$(1$\pi_u$)$_2$(3$\sigma_g$)$_2$(1$\pi_g$)$_1$</td>
<td>−75.333 358</td>
<td>13.012</td>
</tr>
<tr>
<td></td>
<td>b$^2\Delta_g$</td>
<td>88% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\pi_g$)$_1^3$</td>
<td>−75.332 633</td>
<td>13.032</td>
</tr>
<tr>
<td></td>
<td>c$^2\Sigma_g^+$</td>
<td>88% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\sigma_g$)$_1^3$</td>
<td>−75.322 311</td>
<td>13.313</td>
</tr>
<tr>
<td></td>
<td>d$^2\Sigma_g^-$</td>
<td>82% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\sigma_g$)$_1^3$</td>
<td>−75.316 892</td>
<td>13.460</td>
</tr>
<tr>
<td></td>
<td>e$^2\Pi_u$</td>
<td>85% (2$\sigma_u$)$_2$(1$\pi_u$)$_3$(3$\pi_g$)$_1^3$</td>
<td>−75.308 704</td>
<td>13.683</td>
</tr>
</tbody>
</table>

$^a$Main contributing configurations calculated at the optimized geometry of each state. For the sake of clarity, the common part of the configuration, i.e., (1$\pi_u$)$_2$(1$\pi_u$)$_2^3$(3$\sigma_g$)$_2^3$, is omitted, and the configurations contributing to less than 5% are disregarded.

$^b$Calculated ionization energy with respect to the X$^1\Sigma_g^+$ neutral ground state.

$^c$Regarding the main configurations, the photoionizing transitions toward the e$^+$ state can only occur thanks to configuration mixing and are thus expected to be very weak.
beams (beamline) seen as dips in the ionization signal during the energy scan leading to an error on the absolute energy scale of 7 meV. A Gaussian multi-peak least-squares fit was performed to locate the band positions. The fitting point errors were deduced as described in Ref. 17 and convoluted with the energy scale precision. E\textsubscript{i} values were also corrected by the field-induced shift (−7 meV) resulting from the 88 V/cm extraction field used in the spectrometer. The overall accuracy of the ionization energies (E\textsubscript{i}) is estimated at 10 meV (2σ uncertainty).

The \textit{ab initio} calculations on the electronic states of C\textsubscript{2} and C\textsubscript{2}+ were carried out using the internally contracted multireference configuration interaction method with Davidson correction (MRCI+Q) with complete active space self-consistent field (CASSCF) wavefunctions. The CASSCF and MRCI calculations were performed at full valence, namely, with 12 (11 for C\textsubscript{2}+) electrons distributed in 12 orbitals with the 1s orbitals of carbon atoms kept doubly occupied but fully optimized. All calculations were performed using the MOLPRO 2012 package. The potential energy curves of the two lowest electronic states of C\textsubscript{2} and the seven lowest electronic states of C\textsubscript{2}+ were computed as a function of C–C bond length d(C–C). Harmonic vibrational wavenumbers were calculated through the standard MOLPRO procedure using the Hessian and normal modes. Complete basis set (CBS) extrapolations were carried out using the VnZ (n = T, Q, 5, and 6) basis set series. The CASSCF and dynamical correlation (E\textsubscript{CASSCF} + C\textsubscript{Corr}) energies were extrapolated using the E\textsubscript{CASSCF}(CBS) + A × exp(−B × n) and E\textsubscript{Corr}(CBS) + C × n\textsuperscript{2/3} functions, respectively. The calculated energies given in this paper correspond to E(CBS) = E\textsubscript{CASSCF}(CBS) + E\textsubscript{Corr}(CBS). Franck–Condon (FC) spectrum simulations were carried out by means of the PGOPHER software, using our \textit{ab initio} results as input data.\textsuperscript{19}

As reported by several theoretical works,\textsuperscript{19,20,21} the energetic landscape of C\textsubscript{2}+ from its ground state up to only 3 eV is very dense. In Fig. 1, our calculated potential energy surfaces are displayed vs the d(C–C) bond distance for the two lowest electronic states of C\textsubscript{2} and the seven lowest electronic states of C\textsubscript{2}+. The energies calculated at the equilibrium geometries obtained in the VnZ basis sets (n = T, Q, 5, and 6) were extrapolated as a function of the n cardinal number to estimate the CBS limit for each state. The resulting energies with respect to the C\textsubscript{2} ground state energy are reported in Table I.

From Fig. 1 and the main configurations of Table I, only one direct photoionizing transition from the X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−} electronic ground state should be allowed below 14 eV, namely, a\textsuperscript{−} 2\Pi\textsubscript{u} ← X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−}, and six are possible from the a\textsuperscript{3}\Pi\textsubscript{u} metastable state. However, according to Ref. 11, two more photoionizing transitions involving the states of 2\Sigma\textsuperscript{−} symmetry are also expected from the X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−} state through shake-up processes, i.e., c\textsuperscript{−} 2\Sigma\textsuperscript{−} ← X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−} and d\textsuperscript{−} 2\Sigma\textsuperscript{−} ← X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−}. Using the \textit{ab initio} output files of our calculations, we have performed a Franck–Condon (FC) simulation of each transition with the PGOPHER software neglecting spin.\textsuperscript{22} For that purpose, we directly used the MOLDEN output files calculated with AVQZ basis for all states except the d\textsuperscript{−} state (with AVTZ basis) because of convergence issues. The adiabatic energy levels were also implemented in PGOPHER.

These simulations are compared with the experimental TPE spectrum of C\textsubscript{2} in Fig. 2. From this figure, one can readily assign three different photoionizing transitions between 11.4 eV and 12.7 eV:

- X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−}(v\textsuperscript{′}) ← a\textsuperscript{−} 2\Pi\textsubscript{u}(v\textsuperscript{′} = 0),
- a\textsuperscript{−} 2\Pi\textsubscript{u}(v\textsuperscript{′} = 0) ← a\textsuperscript{3}\Pi\textsubscript{u}(v = 0),
- a\textsuperscript{−} 2\Pi\textsubscript{u}(v\textsuperscript{′}) ← X\textsuperscript{1}\Sigma\textsuperscript{g}\textsuperscript{−}(v\textsuperscript{′}).

Above 12.7 eV, the assignment is more complicated due to the numerous vibronic transitions, their weak oscillator strengths, and the low signal-to-noise ratio of the experimental signal. It is, nevertheless, clear that other transitions occur especially around 13 eV, 13.2 eV, and 13.6 eV where net signals are observed. Using the FC simulations of the three assigned transitions and fitting the adiabatic ionization potentials (IPs) and the vibronic band...
The agreement is very satisfactory, strengthening our assignment. To our knowledge, there is no other measurement of \( \Delta E(a'-X') \) in the literature. In addition, we extract the adiabatic IP of the forbidden \( X^+ \Sigma_g^+ \leftarrow X^+ \Sigma_g^+ \) photoionizing transition \( E_i(X^' \leftarrow X) = 11.873(10) \text{ eV} \), in very good agreement with the one derived in 2016 by Krechkivska et al. \[11.866(5) \text{ eV}\]. Using the gas-phase enthalpy of formation of the quadruple ground state of the \( C_2 \) cation at 0 K from the active thermochemical tables \[12-22\] [i.e., \( \Delta H^0(0\text{K})(C_2(\Sigma_g^+)) = 1965.2 \text{ kJ mol}^{-1} \] and our measured \( \Delta E(a'-X') = 54.7(10) \text{ kJ mol}^{-1} \], we determine the enthalpy of formation of the lowest doublet state of the \( C_2 \) cation, \( \Delta H^0(0\text{K})(C_2(3\Pi_u)) = 2019.9(10) \text{ kJ mol}^{-1} \). From the vibrational structures of the \( X^+ \Sigma_g^+ \leftarrow a^3\Pi_u \) and \( a^3\Pi_u \leftarrow X^+ \Sigma_g^+ \) transitions, we also extract the vibrational fundamentals of the \( X^+ \Sigma_g^+ \) and \( a^3\Pi_u \) electronic states of \( C_2^+ \), \( \nu_0(X^+) = 1460(80) \text{ cm}^{-1} \) and \( \nu_0(a^3\Pi_u) = 1590(80) \text{ cm}^{-1} \), respectively.

In addition to these results, the \( C_2 \) ionization yield has been measured and is reported in Fig. 4. Despite the low signal-to-noise ratio, several reproducible structures are observed at 11.814 eV.

From the experimental positions of the origin bands, we can then extract the adiabatic IP for the three allowed-photoionizing transitions. These values corrected by the field-induced Stark shift (\(-7 \text{ meV}\)) are reported in Table II. The adiabatic IP obtained for the \( X^+ \Sigma_g^+ \leftarrow a^3\Pi_u \) transition is in very good agreement with that of Krechkivska et al. \[11.791(5) \text{ eV}\]. In the case of the \( a^2\Pi_u \leftarrow X^+ \Sigma_g^+ \) and \( a^2\Pi_u \leftarrow X^+ \Pi_u \) transitions, no other measurement has been reported in the literature but for this work. Combining the three origin bands, we derive the singlet-triplet and quadruplet-doublet energy differences in the neutral and cationic species, respectively, \( \Delta E(a'-X) = 0.079(10) \text{ eV} \) and \( \Delta E(a'-X') = 0.567(10) \text{ eV} \). Our \( \Delta E(a'-X) \) value is in very good agreement with the zero-point energy derived from the rotationally resolved analysis of Chen et al. \[613.650(3) \text{ cm}^{-1} = 76 \text{ meV}\].

### Table II. Adiabatic ionization energies of \( C_2 \).

<table>
<thead>
<tr>
<th>Transition</th>
<th>( E_{i,\text{calc.}} ) (eV)</th>
<th>( E_{i,\text{calc.}} ) corrected ZPE (eV)</th>
<th>( E_{i,\text{expt.}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X^+ \Sigma_g^+ \leftarrow X^+ \Sigma_g^+ )</td>
<td>\ldots</td>
<td>11.803</td>
<td>11.771</td>
</tr>
<tr>
<td>( a^2\Pi_u \leftarrow X^+ \Sigma_g^+ )</td>
<td>12.40</td>
<td>12.381</td>
<td>12.365</td>
</tr>
<tr>
<td>( c^2\Sigma_g^+ \leftarrow X^+ \Sigma_g^+ )</td>
<td>\ldots</td>
<td>13.313</td>
<td>13.275</td>
</tr>
<tr>
<td>( d^2\Sigma_g^+ \leftarrow X^+ \Sigma_g^+ )</td>
<td>\ldots</td>
<td>13.460</td>
<td>13.413</td>
</tr>
<tr>
<td>( X^+ \Sigma_g^+ \leftarrow a^3\Pi_u )</td>
<td>11.75</td>
<td>11.750</td>
<td>11.733</td>
</tr>
<tr>
<td>( a^2\Pi_u \leftarrow a^3\Pi_u )</td>
<td>12.29</td>
<td>12.328</td>
<td>12.326</td>
</tr>
<tr>
<td>( A^+ \Pi_u \leftarrow a^3\Pi_u )</td>
<td>\ldots</td>
<td>12.959</td>
<td>12.974</td>
</tr>
<tr>
<td>( b^2\Delta_g \leftarrow a^3\Pi_u )</td>
<td>\ldots</td>
<td>12.979</td>
<td>12.953</td>
</tr>
<tr>
<td>( c^2\Sigma_g^+ \leftarrow a^3\Pi_u )</td>
<td>\ldots</td>
<td>13.260</td>
<td>13.236</td>
</tr>
<tr>
<td>( d^2\Sigma_g^+ \leftarrow a^3\Pi_u )</td>
<td>\ldots</td>
<td>13.404</td>
<td>13.374</td>
</tr>
</tbody>
</table>

*CCSD(T) values.

Derived from the complete basis set (CBS) limit extrapolations and corrected by the zero point energies (ZPE) of the neutral and cationic states when indicated.

Resonant two-photon threshold ionization spectroscopy.

Fitted values used in Fig. 3 corrected by the field-induced shift.

Forbidden transition.
The Journal of Chemical Physics

The Journal

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11.89 eV, 12.025 eV, 12.100 eV, 12.145 eV, 12.266 eV, 12.307 eV, 12.443 eV, 12.549 eV, 12.594 eV, and 13.47 eV. We attribute these features to autoionization processes. However, the assignment of the involved Rydberg states is not straightforward. Indeed, in the experiment, the lowest triplet and singlet states of C2 are populated and many electronic states of the cation lie within the explored energy range. Hence, several Rydberg series are superimposed in the spectrum. The autoionization structures have been discussed by Toffoli and Lucchese, but only above 13 eV. The comparison with our experiment is thus not possible. Nevertheless, below 13 eV, the sharpest structures might be the signature of Rydberg series converging toward excited states of the cation above the a' state. These Rydberg series are most probably reached from the triplet metastable state of the neutral, and they autoionize into the X' or the a' cationic states. Note that electronic and vibrational autoionization processes might coexist in this energy range for C2 like in the case of the CH radical.13 Higher resolved ion yield spectra of C2 in its ground state only and in its two lowest electronic states are necessary to study in detail the autoionization processes of this system. In astrophysical models, the photoionization cross section of C2 is assumed to be zero below the estimated IP (12.16 eV) and constant above this energy.12 Although the assignment of this ion yield still has to be performed, the data clearly show that the crude estimated ion yield used in the astrophysical models should be revised.

To conclude, the new results presented in this paper significantly improve the spectroscopic knowledge of the dicarbon cation. They should stimulate future high-resolution experiments employing the present radical source to further refine the values of the ionization energies, to help in identifying the autoionization structures, and to disentangle the vibronic transitions observed above 13 eV.

This work was performed on the DESIRS beamline under Proposal No. 20181543. The authors acknowledge SOLEIL for provision of synchrotron radiation facilities and the DESIRS beamline team for their assistance. This work was supported by the French Agence Nationale de la Recherche (ANR) under Grant No. ANR-12-BS08-0020-02 (Project SYNCHROKIN) and by the Programme National “Physique et Chimie du Milieu Interstellaire” (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES.

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