Supplementary Material for "THE THRESHOLD PHOTOELECTRON SPECTRUM OF THE GEMINAL CHLORO-FLUORO-ETHENE (1,1-C_2H_2FCl) ISOMER. EXPERIMENT AND THEORY."

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Description of the "subtraction procedure".

The subtraction procedure referred to in section 2.2 consists of two steps:
(i) The "smoothing" step: the first decision to take is the number of points at a time to be considered in the smoothing routine applied to the experimental curve. The smoothing itself is obtained by removing Fourier components with "frequencies" higher than $1/n.\Delta t$ where n is the number of data points considered at a time and Δt is the abscissa spacing

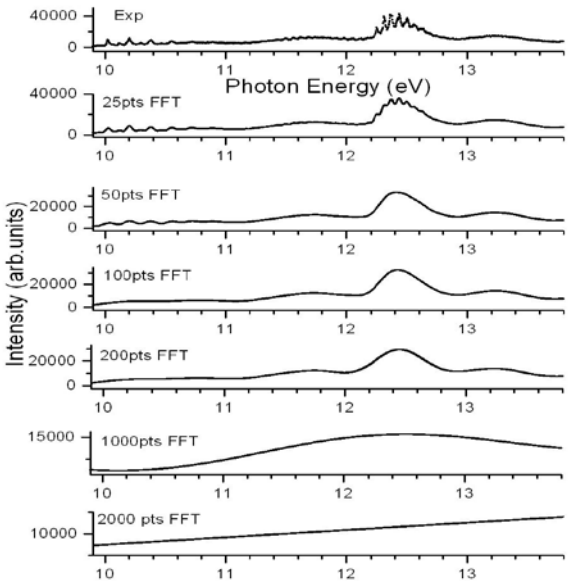

FIG.1.

between two adjacent data points. As shown in **Fig.1**, several trials on an experimental curve are presented. Up from "100 pts FFT" the fine structure disappears and is chosen for the next step.

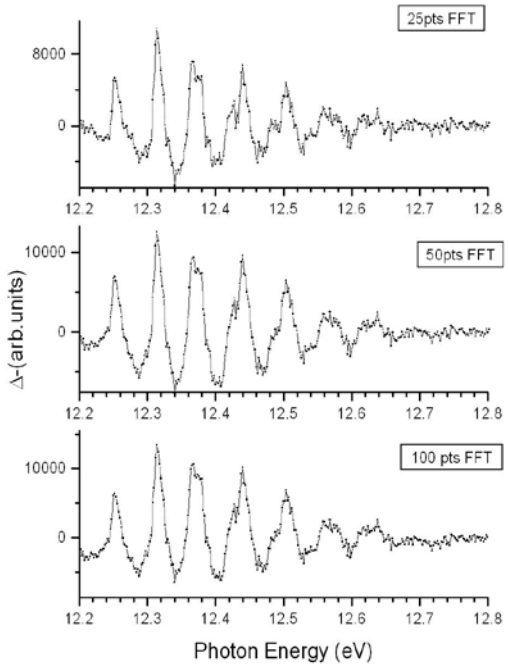

FIG. 2.

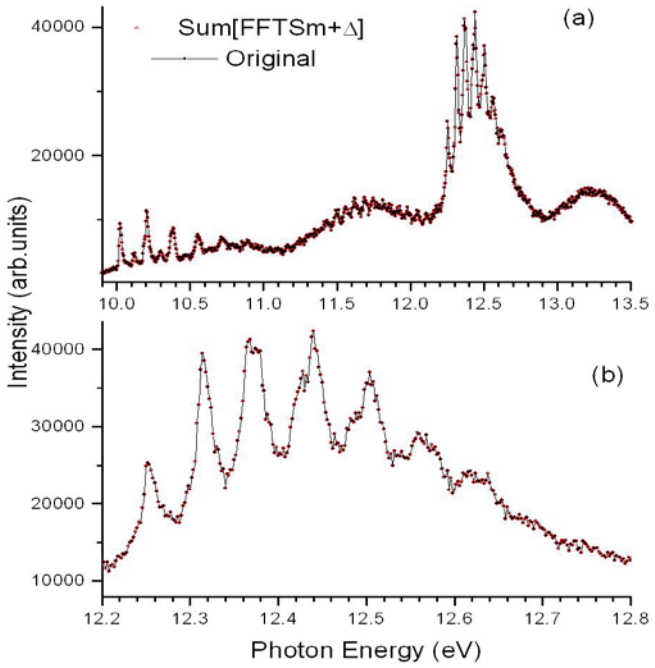

FIG. 3.

(ii) The "subtraction" step: The result of this smoothing is subtracted numerically point by point from the original data. The result is represented in **Fig.2** for different smoothing as focused on a particular energy region.

That no "spurious peaks" appear during this processing can be checked by summing the results of "step (i)" and "step (ii)" and by verifying that it overlaps point by point with the original experimental data (see **Fig.3a and 3b**). No point is lost during the process as shown in **Fig.3**. If any "spurious peak had appeared during this processing in any energy range, the "sum" and the "original" could not overlap in this energy range.

TABLE S1: Optimized geometries of the neutral and of the ionic ground states and the first two cationic excited states in the C_S symmetry group at different calculation levels. Internuclear distances in Å and angles in degrees [1].

Neutral Ground State - $\tilde{X}$ ^{1}A'					
Level	C1-C2	C2-H3	C2-H4	C1-F5	C1-Cl6
CCSD(FC)	1.3374	1.0917	1.0894	1.3498	1.7324
M06-2X	1.3231	1.0865	1.084	1.333	1.7251
	H3-C2-C1	H4-C2-C1	F5-C1-C2	Cl6-C1-C2	
CCSD(FC)	119.398	120.192	122.255	126.035	
M06-2X	119.163	120.133	122.876	125.739	
Cation Ground State - $\tilde{X}$ ^{2}A″					
Level	C1-C2	C2-H3	C2-H4	C1-F5	C1-Cl6
CCSD(FC)	1.4214	1.0956	1.0938	1.293	1.6558
M06-2X	1.4098	1.0912	1.0893	1.2816	1.6497
	H3-C2-C1	H4-C2-C1	F5-C1-C2	Cl6-C1-C2	
CCSD(FC)	118.776	119.619	118.636	124.15	
M06-2X	118.726	119.667	119.085	123.962	
Cation First Excited State - $\tilde{A}$ ^{2}A'					
Level	C1-C2	C2-H3	C2-H4	C1-F5	C1-Cl6
CCSD(FC)	1.3211	1.0965	1.0926	1.308	1.8741
M06-2X	1.3056	1.0942	1.0896	1.2891	1.879
	H3-C2-C1	H4-C2-C1	F5-C1-C2	Cl6-C1-C2	
CCSD(FC)	117.496	122.278	135.404	120.092	
M06-2X	117.366	122.706	136.75	118.469	
Cation Second Excited State - $\tilde{B}$ ^{2}A"					
Level	C1-C2	C2-H3	C2-H4	C1-F5	C1-Cl6
TD-DFT	1.3244	1.0959	1.0891	1.2617	2.0725
	H3-C2-Cl	H4-C2-C1	F5-C1-C2	Cl6-C1-C2	
TD-DFT	116.99	121.78	135.46	120.36	

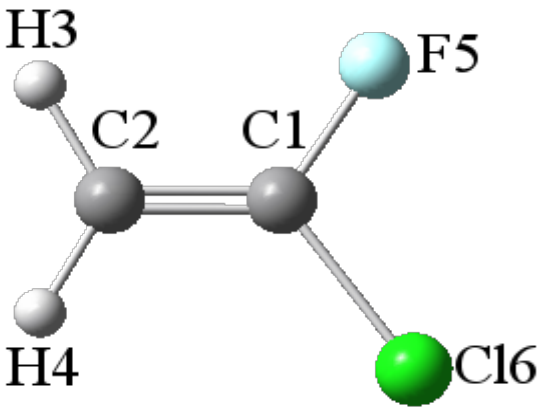

TABLE S2: Wavenumbers (cm^{-1}) related to the vibrational normal modes of 1,1-C_2H_2FCl in its ground state and of 1,1-$C_2H_2FCl^+$ in its ground $\tilde{X}\,^2A''$ and two first excited $\tilde{A}\,^2A'$ and $\tilde{B}\,^2A''$ states as calculated at the M06-2X level ($\tilde{X}$ and $\tilde{A}$ states) and TDDFT ($\tilde{B}$ state). The values are corrected by a scaling factor of 0.96 [1].

State	$\tilde{X}\,^1A'$	$\tilde{X}\,^2A''$	$\tilde{A}\,^2A'$	$\tilde{B}\,^2A''$
Vibr.N..M.[a] a' Symm				
ν_1	3195	3193	3123	3178
ν_2	3082	3062	3001	3080
ν_3	1684	1479	1766	2959
ν_4	1335	1372	1316	1338
ν_5	1161	1298	1061	1254
ν_6	924	953	881	951
ν_7	676	746	472	520
ν_8	416	443	335	272
ν_9	355	350	220	178
a'' Symm				
ν_{10}	865	920	876	892
ν_{11}	698	543	660	409
ν_{12}	509	351	438	402

[a] The respective vibrational motions of the neutral ground state and of the three ionic states are drawn in Fig. 2 in ref. [1] and in Figs. S1-S3 in the present work respectively.

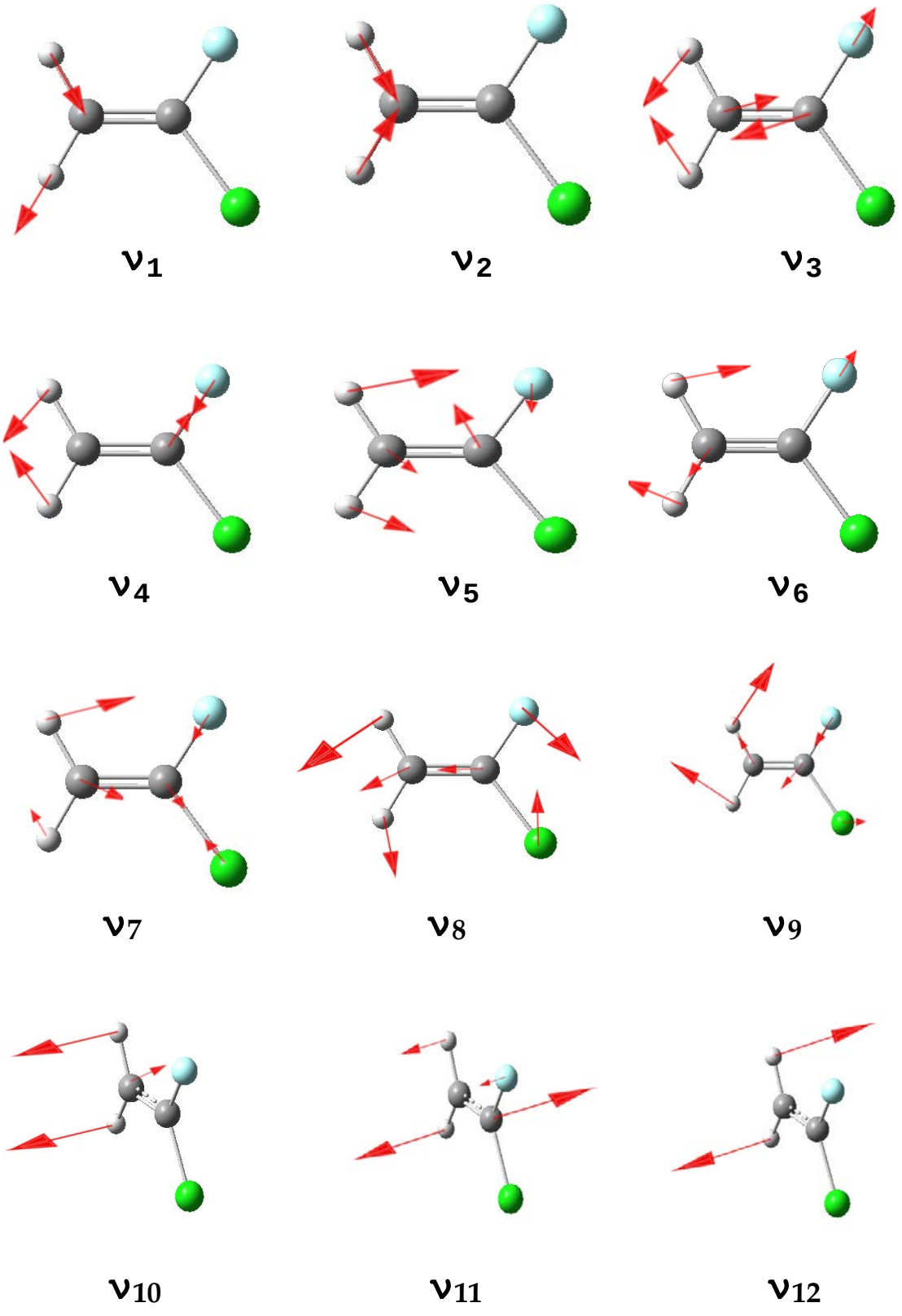

FIG.S1: Schematic representation of the twelve vibrational normal modes of 1,1-$C_2H_2FCl^+$ as calculated in the present work for the $\tilde{X}\,^2A''$ state.

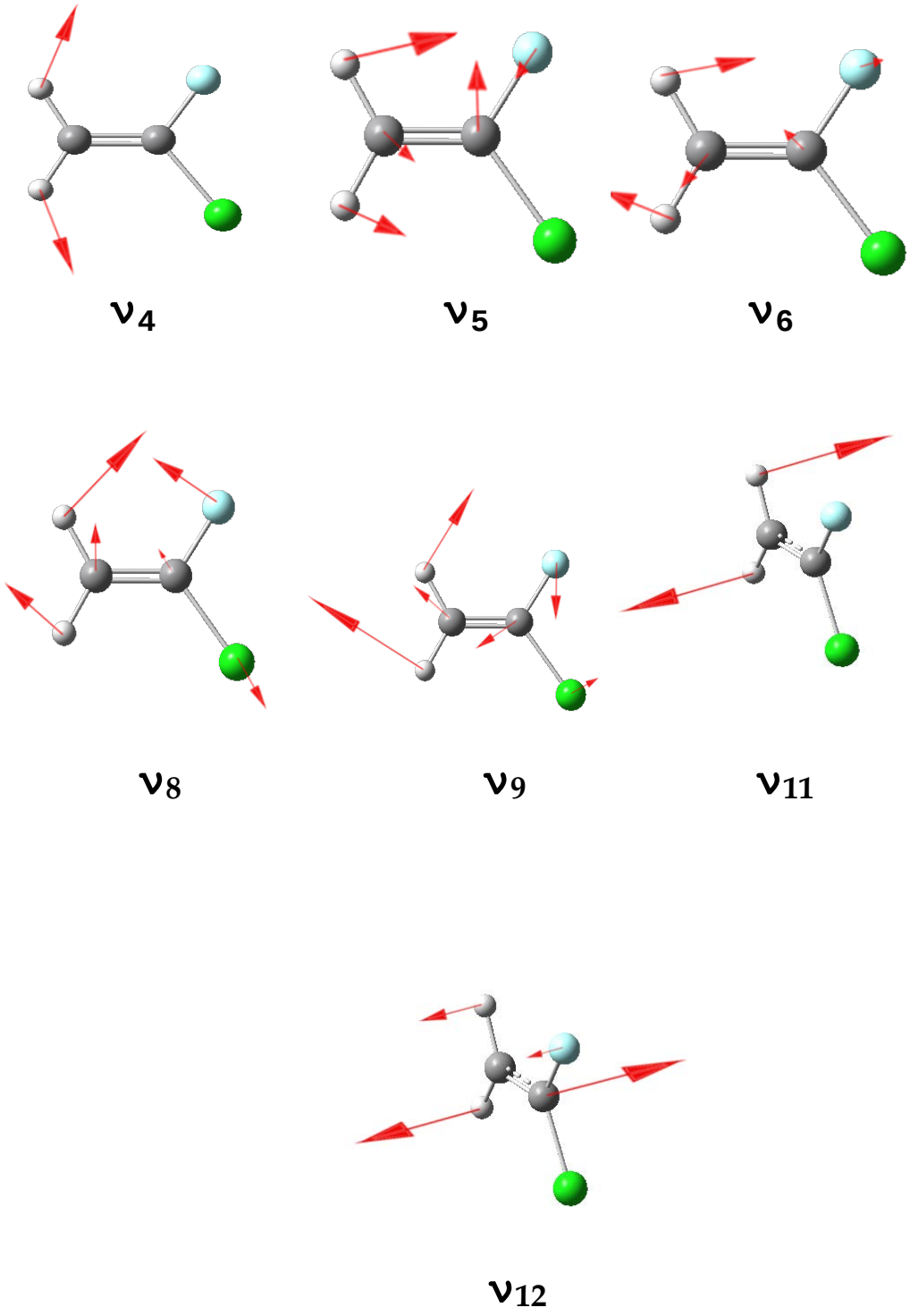

FIG.S2: Schematic representation of the seven vibrational normal modes of 1,1-$C_2H_2FCl^+$ $\tilde{A}\,^2A'$ differing from those of the $\tilde{X}\,^2A''$ state.

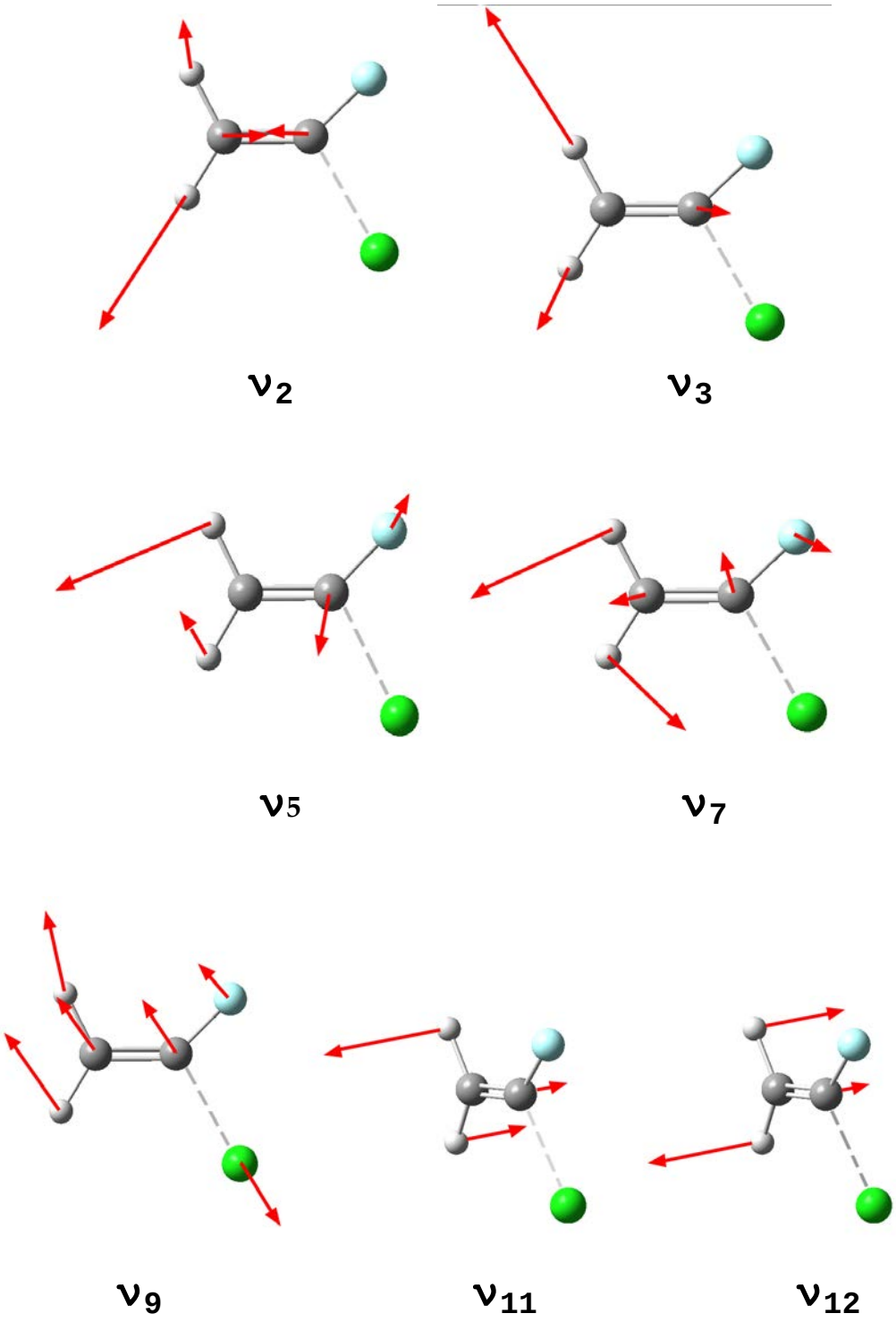

FIG.S3: Schematic representation of the seven vibrational normal modes of 1,1-$C_2H_2FCl^+$ $\tilde{B}\,^2A''$ differing from those of the $\tilde{X}\,^2A''$ state.