Supporting Information for

Infrared Spectroscopy of Gold Carbene Cation (AuCH$_2^+$): Covalent or Dative Bonding?

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Table S1 provides information needed to calculate the rotational contours: dipole derivatives, principle axes, and moments of inertia of [Au,C,2H]$^+$. Figure S1 shows representative mass spectra of the ionic species formed from gold laser ablation in a flow of ethylene oxide mixed with He with and without laser irradiation at 1010 cm^{-1}. Figure S2 illustrates the geometric orientation of the Cartesian principle axes used in the calculation of dipole derivatives and moments of inertia of the ground state of AuCH$_2^+$. Figure S3 shows the spectra for AuCH$_2^+$ ($^1A_1$) including rotational band structure at 293 K both with and without including nuclear spin statistics. Figure S4 shows representative mass spectra of the ionic species formed from gold laser ablation in a flow of ethylene oxide mixed with He with and without laser irradiation at 836 cm^{-1}. Figure S5 shows the spectrum for AuCH$_2^+$ ($^1A_1$) including the rotational band contours and the two lowest frequency bands blue-shifted by 90 cm^{-1}. Figures S6 and S7 show comparisons of the calculated spectra for alternative precursors with the experimental spectrum.

Table S1. Dipole Derivatives, Principle Axes, and Moments of Inertia of $AuCH_2^+$ ($^1A_1$)

| Frequency (cm^{-1})	Coordinate 1	Coordinate 2	Coordinate 3	IR Intensity (km mol^{-1})
648.26	-2.39E-10	-1.61E-10	6.06E+00	36.734
758.59	-7.79E-10	4.59E+00	1.40E-10	21.059
1030.07	8.10E+00	-5.89E-10	-5.56E-10	65.627
1393.35	1.90E-10	1.40E-10	-3.26E+00	10.612
3077.32	4.59E-10	-3.62E-10	-4.45E+00	19.828
3197.60	5.51E-10	6.59E+00	1.92E-10	43.419
Eigenvalues	6.18177	184.98131	191.16308	
X	0	0	1	
Y	0	1	0	
Z	1	0	0	
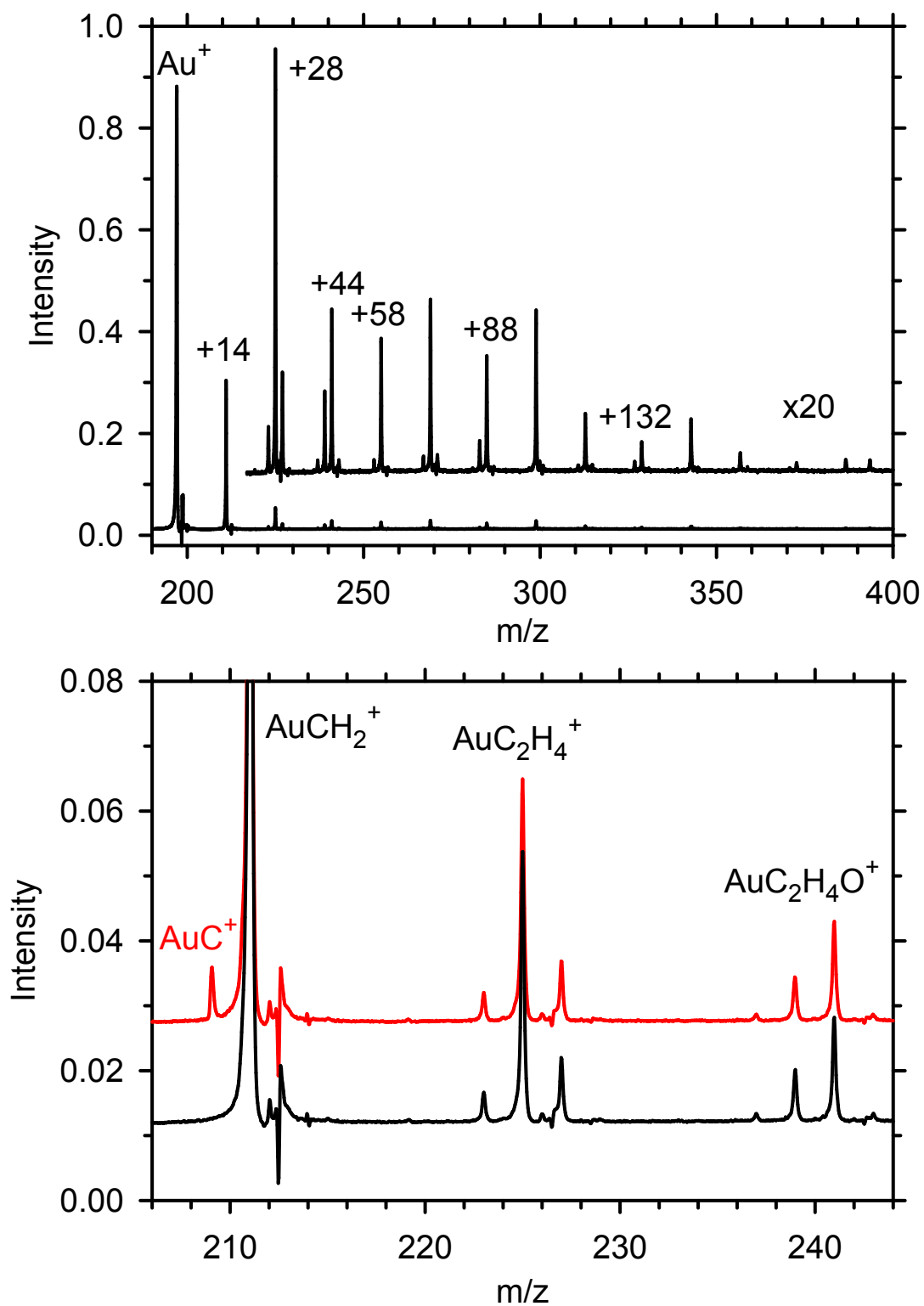
Figure S1. Mass spectrum of the ionic species formed from laser ablation of gold in a flow of ethylene oxide mixed with He as observed with no laser light (black trace) and with laser light (red trace) at 1010 cm^{-1}. Note the appearance of AuC$^+$ in the red trace.
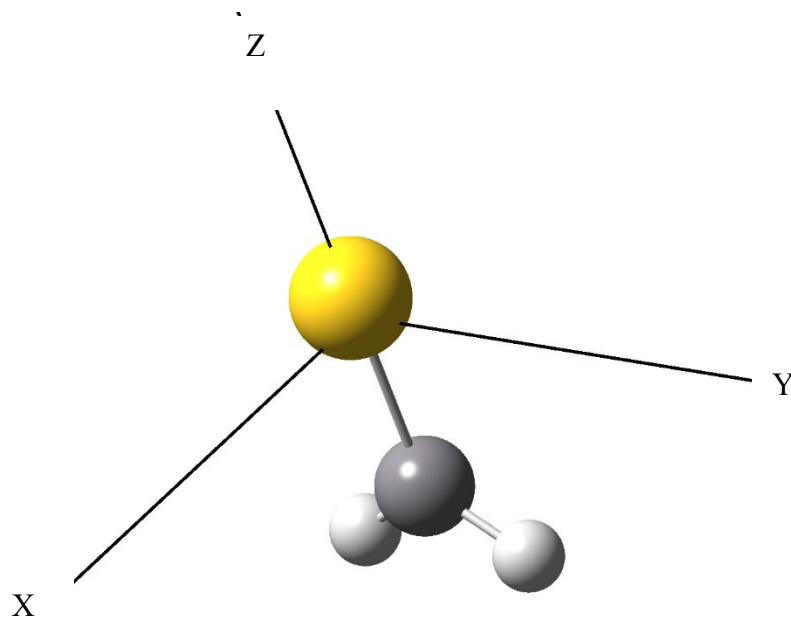
Figure S2. Geometric orientation of the Cartesian principle axes for which dipole derivatives and moments of inertia of $AuCH_2^+$ ($^1A_1$) were calculated.
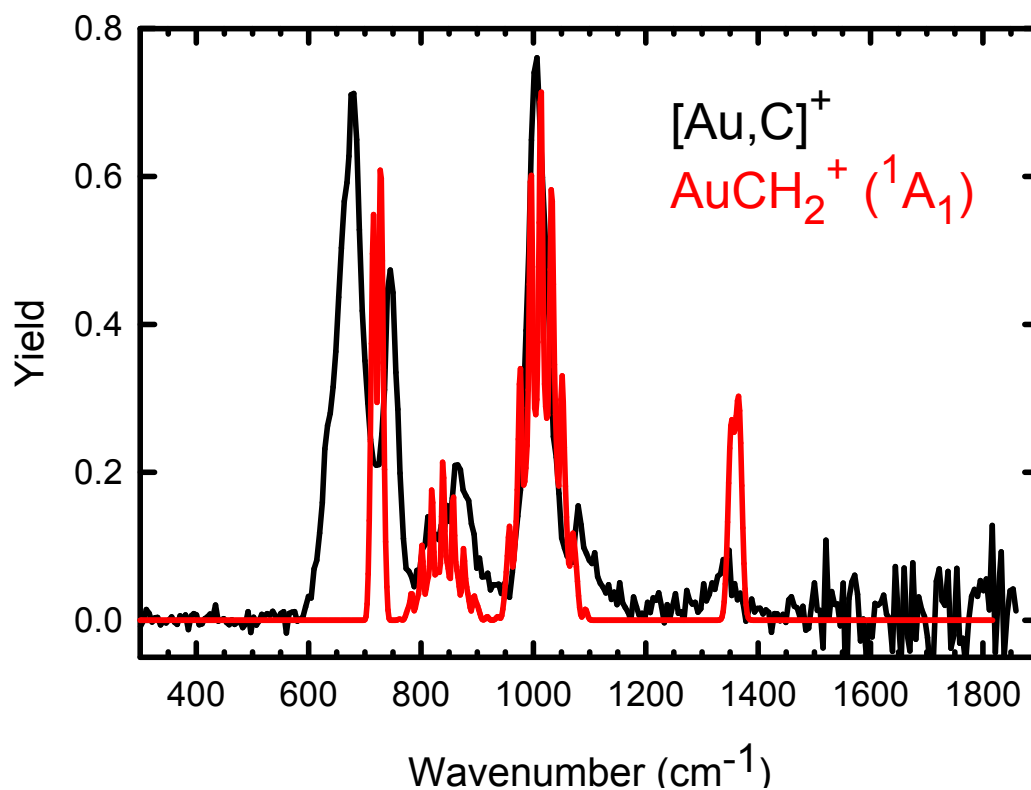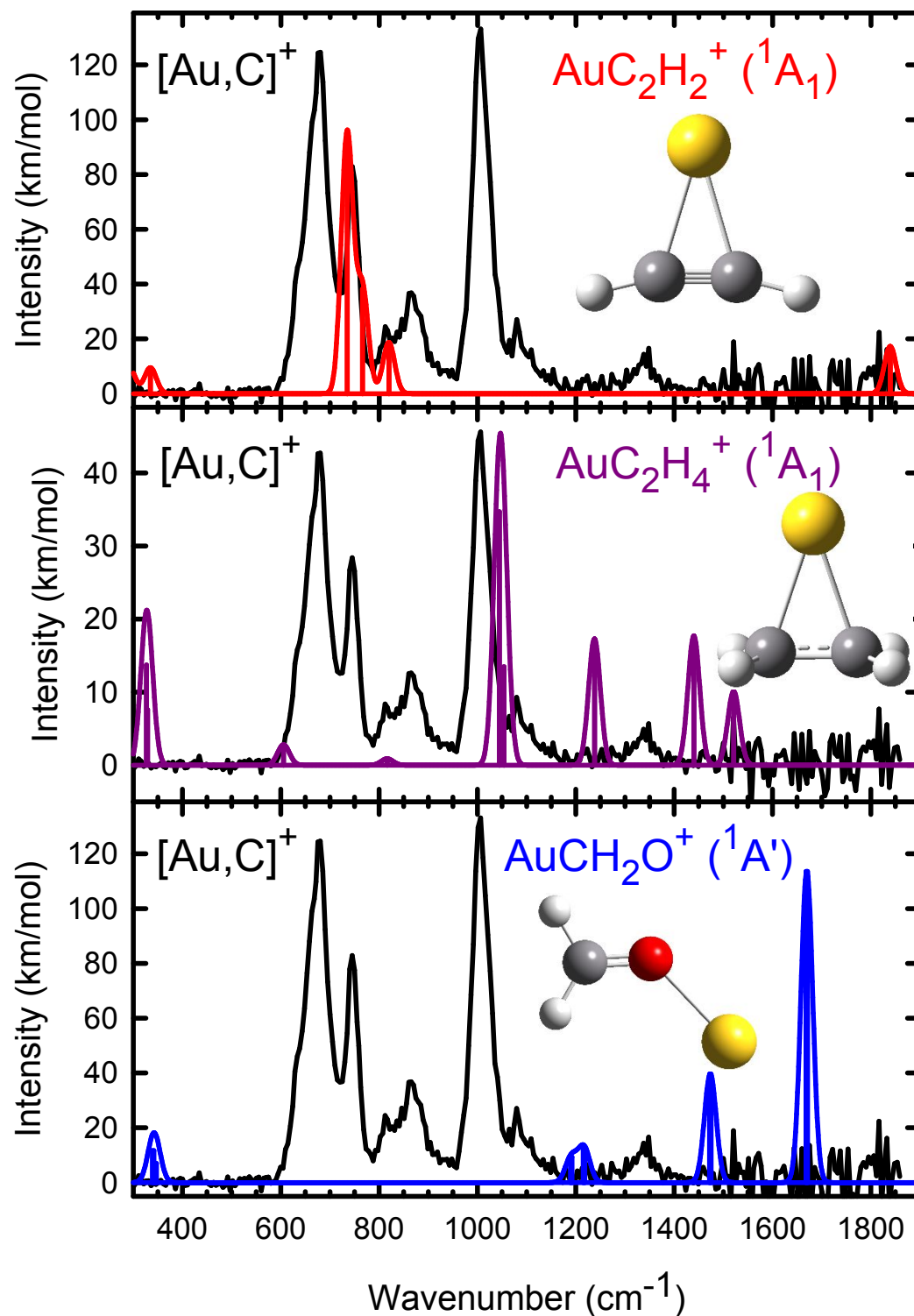

Figure S4. IRMPD spectrum for formation of $[Au,C]^+$ (black) and the DFT calculated spectra including rotational band structure at 77 K for the singlet carbene $AuCH_2^+$ (red) with the two lowest frequency bands blue-shifted by 90 cm^{-1}.
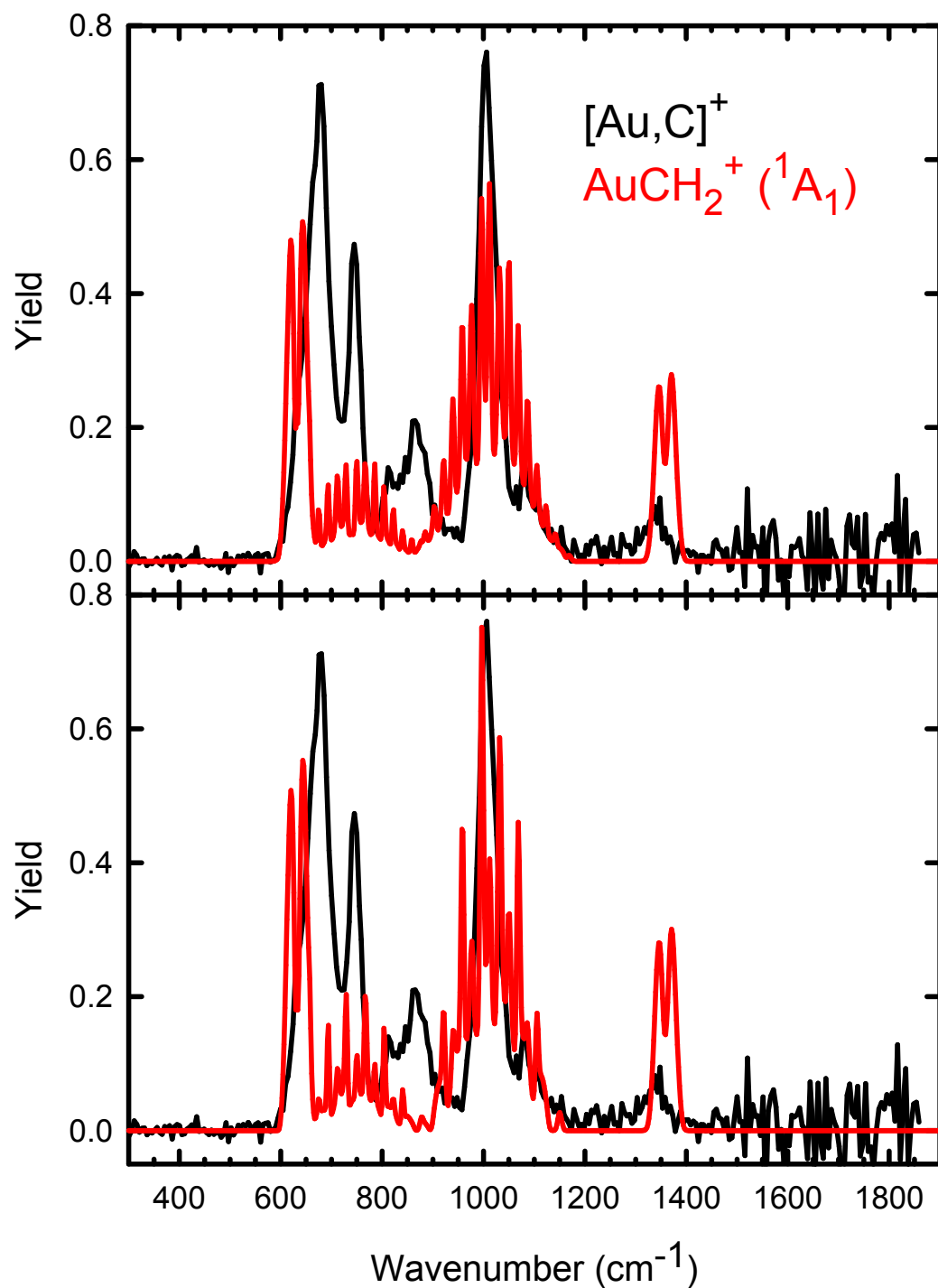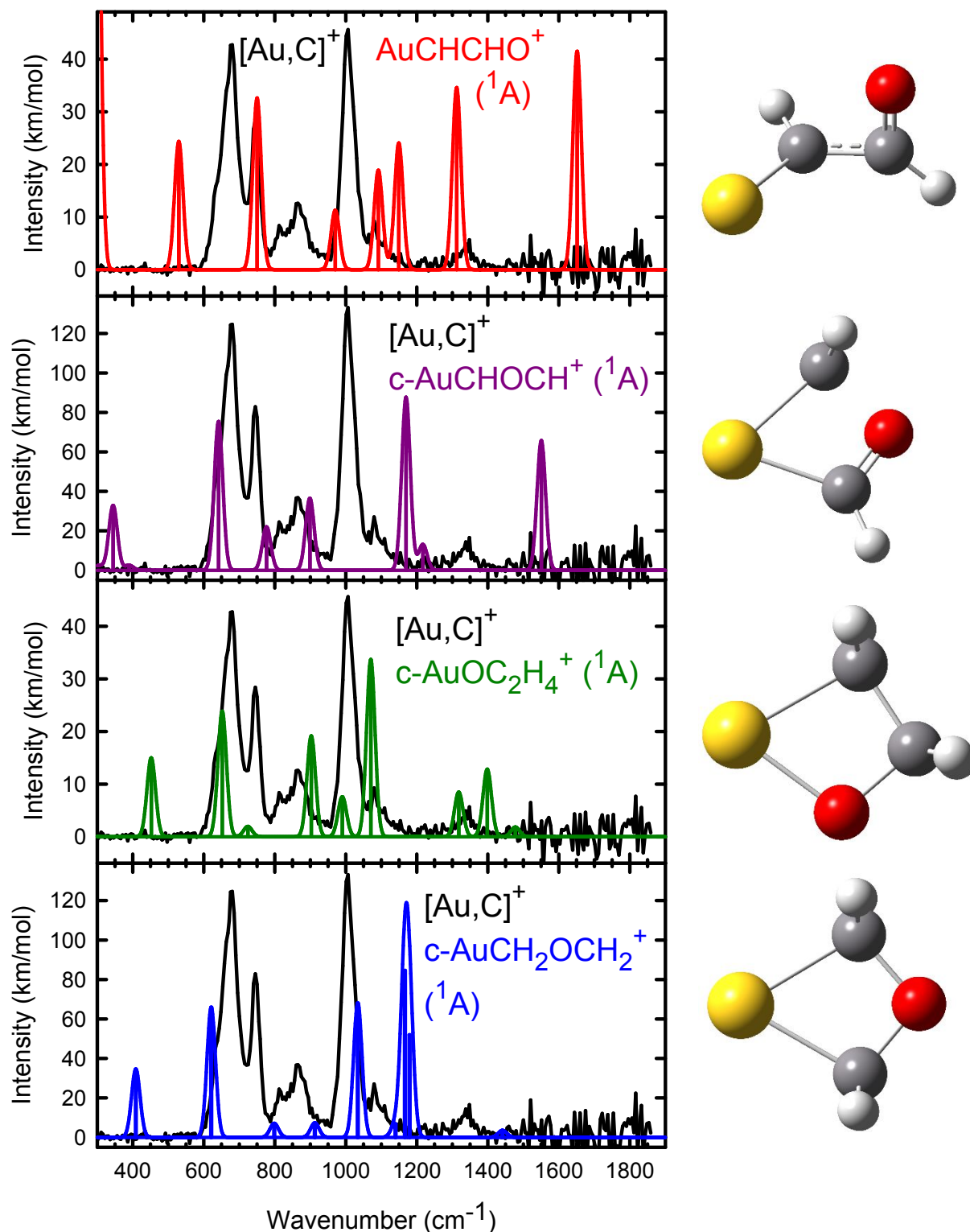
Figure S3. IRMPD spectra for formation of [Au,C]$^+$ (black) and the DFT calculated spectra including rotational band structure at 293 K excluding (top panel) and including (bottom panel) nuclear spin statistics for the singlet carbene AuCH$_2^+$ (red).
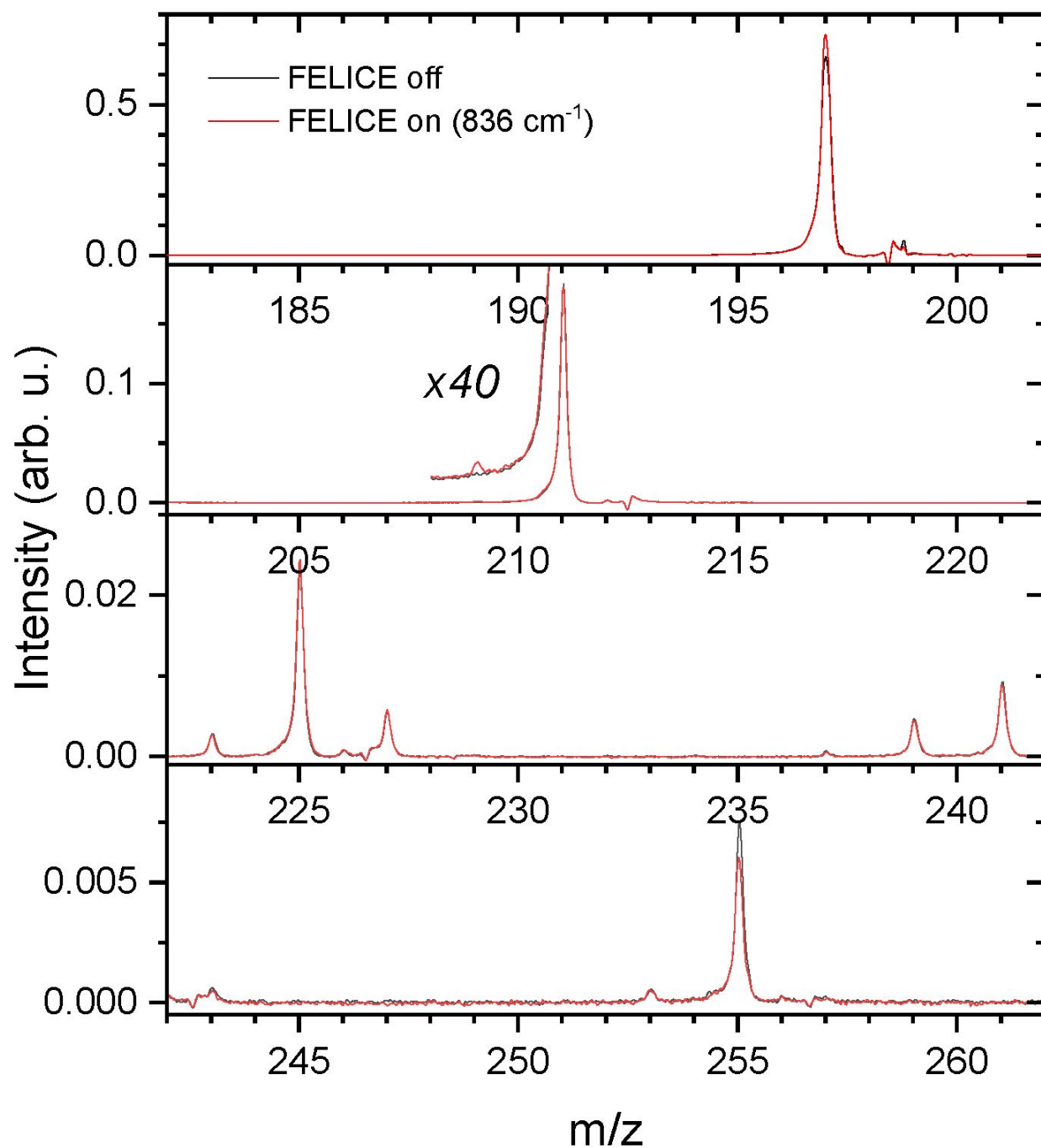
Figure S5. Mass spectrum of the ionic species formed from laser ablation of gold in a flow of ethylene oxide mixed with He as observed with no laser light (black trace) and with laser light (red trace) at 836 cm^{-1}. Note the appearance of AuC$^+$ at *m/z* 209 (seen in the expansion) and the depletion of the peak at *m/z* 255, AuC$_3$H$_6$O$^+$.

Figure S6. IRMPD spectra for formation of [Au,C]$^+$ (black) and the DFT calculated spectra for the metallacyclopropene, AuC$_2$H$_2^+$ (^{1}A$_1$) (top trace, red), metallacyclopropane, AuC$_2$H$_4^+$ (^{1}A$_1$) (middle trace, purple), and gold formaldehyde, AuCH$_2$O$^+$ (bottom trace, blue).

Figure S7. IRMPD spectra for formation of [Au,C]$^+$ (black) and the DFT calculated spectra for AuCHCHO$^+$ (^{1}A) (top trace, red), metallacyclobutene, c-AuCHOCH$^+$ (^{1}A) (middle trace, purple), and metallacyclobutanes, c-AuOC$_2$H$_4^+$ (^{1}A) (middle trace, green) and c-AuCH$_2$OCH$_2^+$ (^{1}A) (bottom trace, blue). Structures are shown to the right.