Supporting Information

Infrared Spectroscopy of the Mass 31 Cation: Protonated Formaldehyde vs Methoxy

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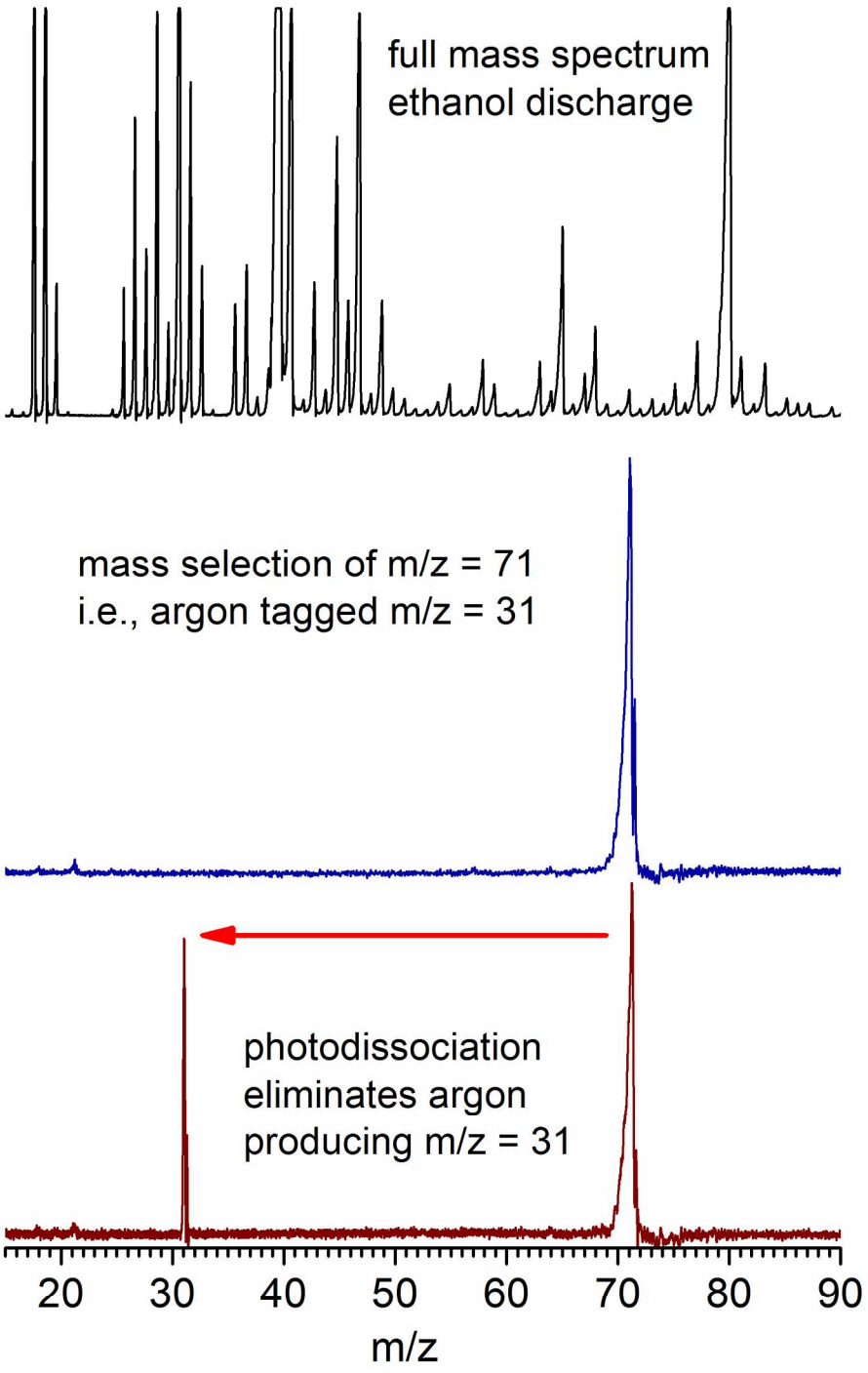

Figure S1. The mass spectrum produced from an ethanol discharge (top trace). The middle trace shows the mass-selected m/z = 71 ion corresponding to the m/z = 31 ion tagged with argon. the bottom trace shows the photodissociation of the m/z=71 ion, which proceeds by elimination of argon to produce m/z=31. This fragment ion is recorded as a function of the IR wavelength to produce a spectrum.

Table S1. Absolute and relative (to lowest energy isomer) energies of structural isomers of the mass 31 cation without argon at the RMP2 (fc) and DFT /B3LYP levels of theory. The cc-pVTZ basis set was used for all atoms. Absolute energies are in atomic units. Relative energies are in kcal/mol and are corrected for zero point energies.

Isomer	MP2 Energy	ΔE	B3LYP Energy	ΔE
CH_2OH^+	-114.5895466	0.0	-114.8335641	0.0
$CHOH_2^+$	-114.4573910	+81.1	-114.7059009	+78.3
$^3CH_3O^+$	-114.4365282	+91.3	-114.7101248	+72.8

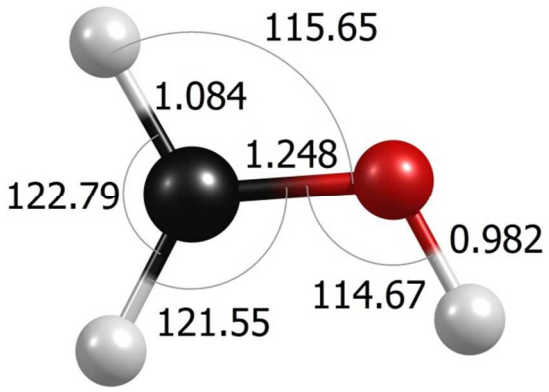

Figure S2. The optimized geometry of protonated formaldehyde (CH_2OH^+) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of protonated formaldehyde (CH_2OH^+) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

1052.7 (109.3), 1122.4 (77.2), 1265.5 (16.2), 1394.7 (97.3), 1508.1 (44.5), 1690.3 (31.7), 3149.0 (5.2), 3299.5 (26.1), 3605.3 (338.5)

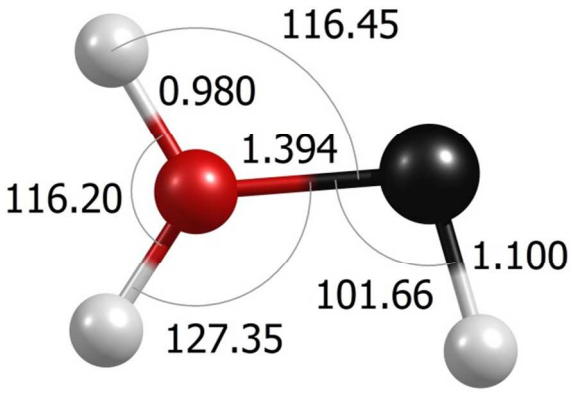

Figure S3. The optimized geometry of oxonio-methylene cation ($CHOH_2^+$) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of oxonio-methylene cation ($CHOH_2^+$) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

548.5 (327.9), 960.2 (54.2), 960.5 (109.6), 991.8 (16.7), 1452.8 (39.2), 1665.4 (116.2), 3081.9 (2.3), 3512.2 (249.7), 3651.5 (491.3)

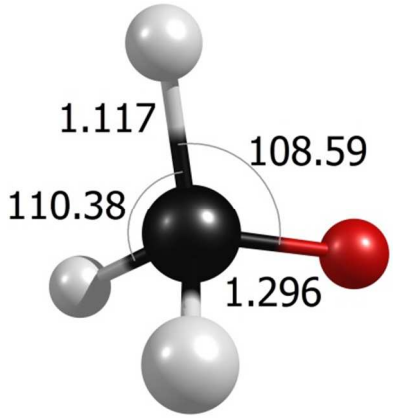

Figure S4. The optimized geometry of triplet methoxy cation ($^3CH_3O^+$) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation ($^3CH_3O^+$) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

818.6 (17.6), 818.8 (17.5), 1128.5 (318.1), 1164.2 (63.1), 1164.2 (63.1), 1267.7 (68.4), 2766.8 (341.9), 2833.5 (161.2), 2834.4 (161.3)

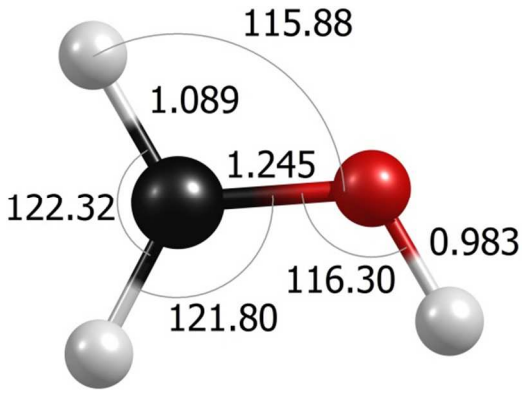

Figure S5. The optimized geometry of protonated formaldehyde (CH_2OH^+) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of protonated formaldehyde (CH_2OH^+) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

1020.1 (115.7), 1111.2 (75.5), 1246.0 (13.8), 1377.5 (110.4), 1479.3 (49.8), 1665.2 (45.1), 3076.3 (3.8), 3216.7 (23), 3571.6 (294.8)

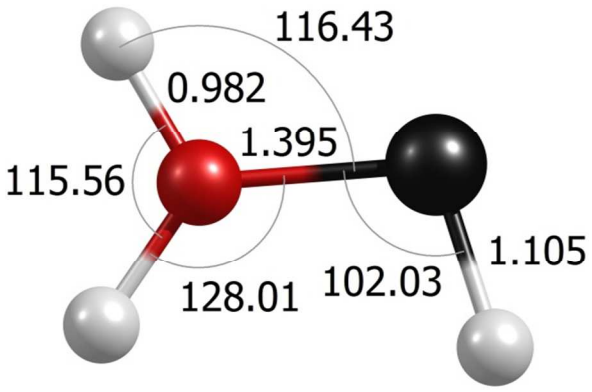

Figure S6. The optimized geometry of oxonio-methylene cation ($CHOH_2^+$) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of oxonio-methylene cation ($CHOH_2^+$) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

587.6 (315.8), 913.9 (91.3), 938.9 (42.4), 988.3 (36.2), 1431.8 (39.6), 1656.2 (97.7), 2995.2 (3.5), 3406.6 (151.8), 3584.6 (439.4)

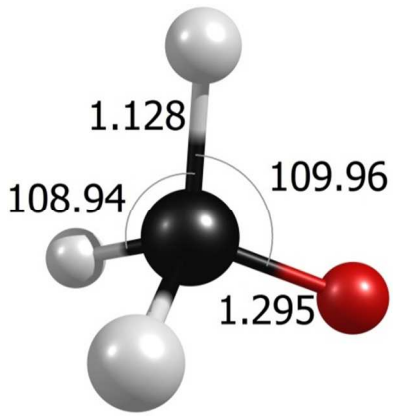

Figure S7. The optimized geometry of triplet methoxy cation ($^3CH_3O^+$) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation ($^3CH_3O^+$) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

854.8 (9.8), 855.5 (9.8), 1124.9 (59.3), 1125.2 (59.3), 1235.0 (177.3), 1243 (33.9), 2686.3 (231.7), 2694.4 (146.8), 2694.5 (146.8)

Table S2. Absolute and relative(to lowest energy isomer) energies of structural isomers of the mass 31 cation with argon at the RMP2 (fc) and DFT /B3LYP levels of theory. The cc-pVTZ basis set was used for all atoms. Absolute energies are in atomic units. Relative energies are in kcal/mol and are corrected for zero point energies. Binding energies (B.E.) of argon are corrected for zero point energies and basis set superposition errors.

Isomer	MP2 Energy	ΔE	B3LYP Energy	ΔE	B.E. Ar (MP2)
CH_2OH^+-Ar	-641.6155647	0.0	-642.3997220	0.0	4.4
$CHOH_2^+$-Ar	-641.4855947	+79.8	-642.2744260	+76.9	5.7
$^3CH_3O^+$-Ar 1	-641.4588957	+93.3	-642.2748899	+73.8	2.1
$^3CH_3O^+$-Ar 2	-641.4581750	+93.7	-642.2715488	+75.5	1.6
$^3CH_3O^+$-Ar 3	-641.4582455	+93.9	-642.2733147	+75.1	1.7

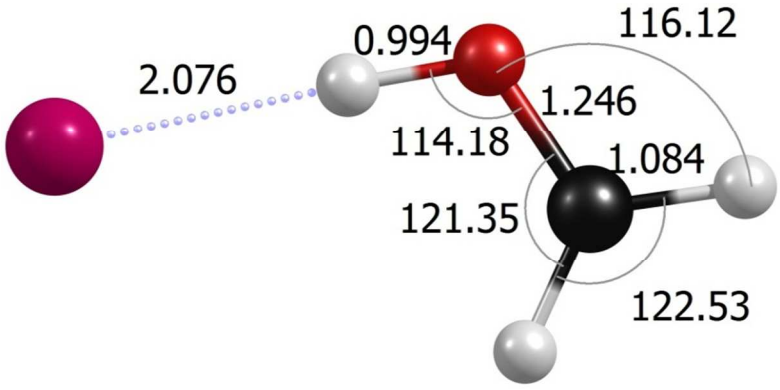

Figure S8. The optimized geometry of protonated formaldehyde with argon (CH_2OH^+-Ar) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of protonated formaldehyde with argon (CH_2OH^+-Ar) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

76.6 (26.0), 161.4 (18.3), 213.9 (22.3), 1107.1 (74.4), 1153.3 (36.0), 1263.6 (15.2), 1414.9 (82.5), 1510.5 (40.6), 1699.9 (34.3), 3146.6 (2.4), 3295.6 (7.8), 3353.7 (1277.5)

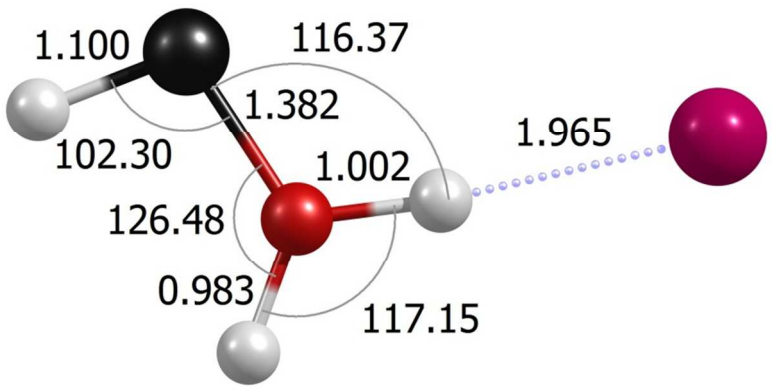

Figure S9. The optimized geometry of oxonio-methylene cation with argon ($CHOH_2^+$-Ar) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of oxonio-methylene cation with argon ($CHOH_2^+$-Ar) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

92.9 (1.2), 201.0 (98.6), 248.3 (110.8), 651.4 (174.5), 1008.3 (117.6), 1011.2 (33.7), 1041.5 (7.3), 1452.3 (23.2), 1658.0 (58.1), 3079.5 (24.5), 3176.1 (1753.7), 3561.9 (374.6)

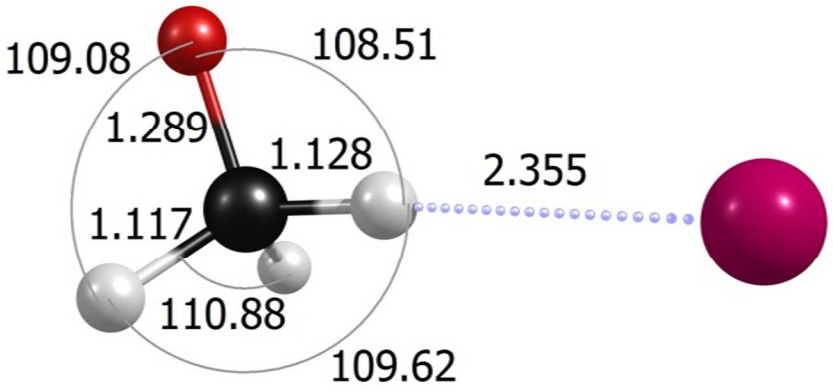

Figure S10. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 1) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 1) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

55.1 (4.3), 102.1 (63.7), 123.3 (0.7), 809.4 (32.6), 822.1 (13.5), 1130.4 (248.0), 1138.6 (50.7), 1170.6 (241.7), 1268.4 (27.4), 2641.6 (773.4), 2792.9 (252.8), 2838.5 (154.9)

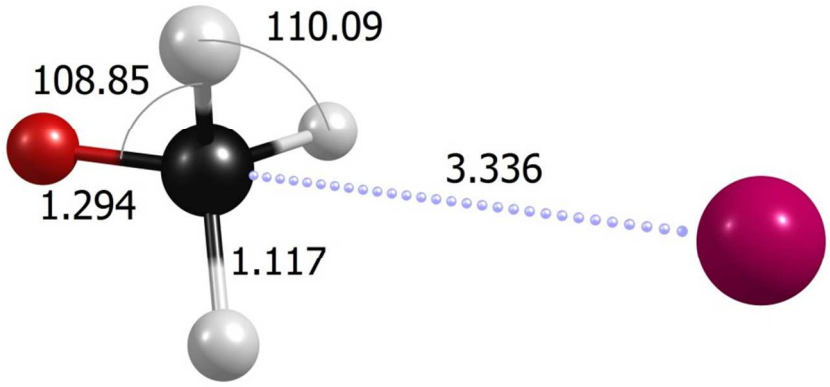

Figure S11. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 2) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 2) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

38.0 (22.9), 38.0 (22.9), 69.6 (22.8), 815.1 (19.7), 815.1 (19.7), 1126.8 (376.4), 1150.4 (56.1), 1150.4 (56.1), 1259.0 (63.2), 2766.6 (351.4), 2829.1 (151.8), 2829.1 (151.8)

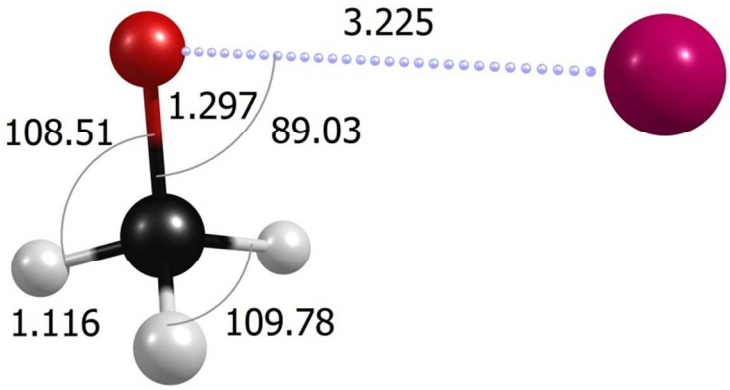

Figure S12. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 3) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 3) calculated at the RMP2 (fc) level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

46.7 (0.3), 68.5 (0.2), 78.4 (37.7), 818.6 (16.5), 823.3 (21.3), 1121.9 (287.8), 1168.3 (79.8), 1169.9 (66.1), 1269.9 (77.3), 2773.7 (325.4), 2837.0 (151.6), 2850.8 (156.5)

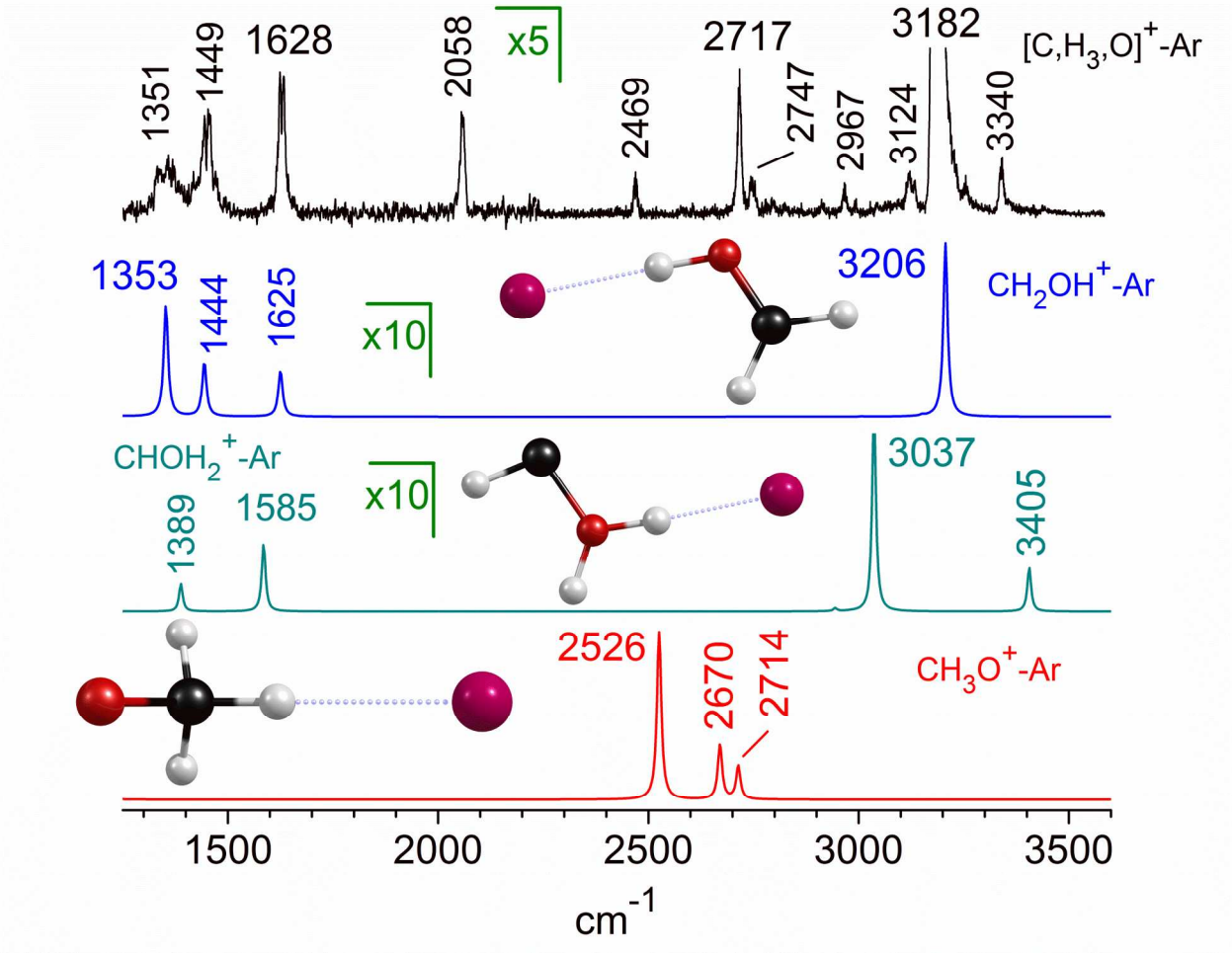

Figure S13. Comparison of the IR-PD spectrum of the mass 31 cation with argon (top trace) with vibrational frequencies (scaled) of three structural isomers computed at the RMP2 (fc) level of theory. Relative energies are available in Table S2.

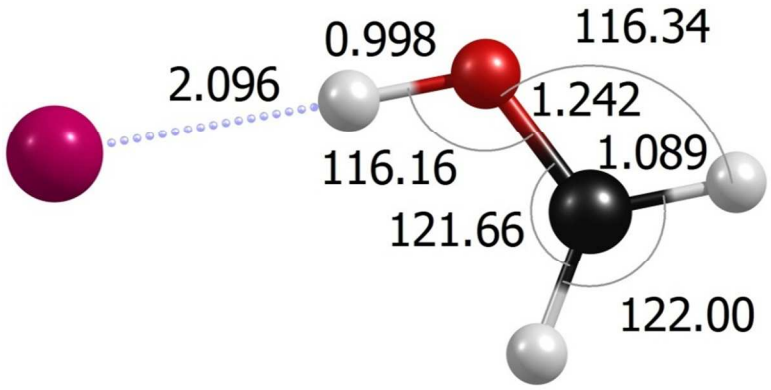

Figure S14. The optimized geometry of protonated formaldehyde with argon (CH_2OH^+-Ar) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Å ngstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of protonated formaldehyde with argon (CH_2OH^+-Ar) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

83.9 (26.9), 159.5 (17.0), 208.1 (19.4), 1073.3 (78.0), 1140.8 (35.9), 1245.5 (12.2), 1394.7 (92.5), 1482.6 (47.1), 1678.8 (53.4), 3074.8 (0.9), 3212.9 (8.9), 3272.1 (1317.7)

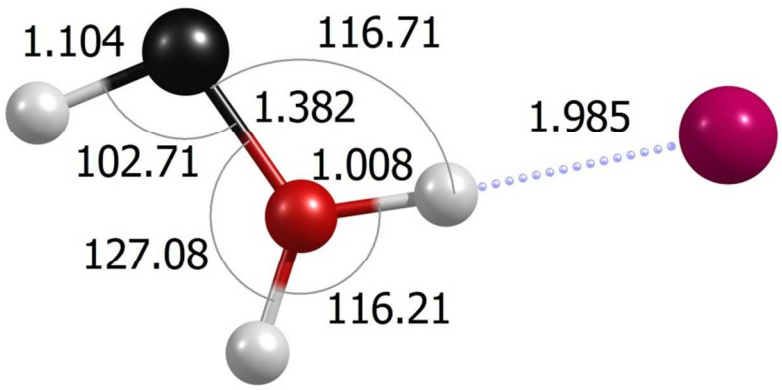

Figure S15. The optimized geometry of oxonio-methylene cation with argon ($CHOH_2^+$-Ar) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of oxonio-methylene cation with argon ($CHOH_2^+$-Ar) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

94.7 (0.8), 195.5 (94.6), 246.8 (96.0), 681.8 (170.1), 967.3 (93.0), 988.3 (35.5), 1036.8 (17.6), 1431.8 (20.1), 1648.2 (46.5), 2995.3 (40.3), 3067.7 (1816.5), 3437.2 (240.5)

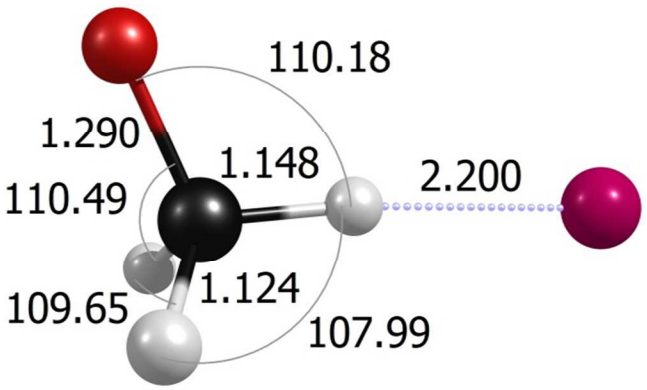

Figure S16. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 1) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 1) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

81.2 (5.2), 140.0 (86.6), 180.7 (0.8), 866.5 (4.0), 886.5 (4.5), 1129.2 (37.6), 1131.1 (99.0), 1244.9 (173.0), 1269.6 (32.3), 2445.0 (1028.0), 2712.0 (181.6), 2735.7 (120.2)

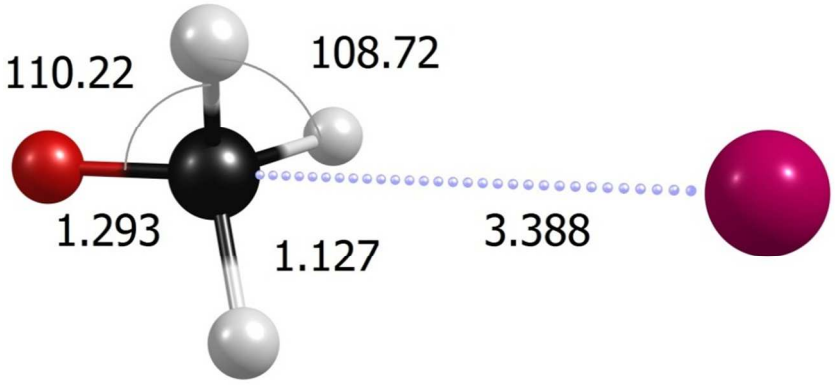

Figure S17. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 2) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 2) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

-61.3 (29.2), -61.3 (29.2), 68.2 (25.1), 849.7 (10.6), 849.7 (10.5), 1116.6 (52.3), 1116.7 (52.3), 1223.1 (259.8), 1244.2 (0.0), 2691.0 (215.2), 2692.9 (132.7), 2692.9 (132.7)

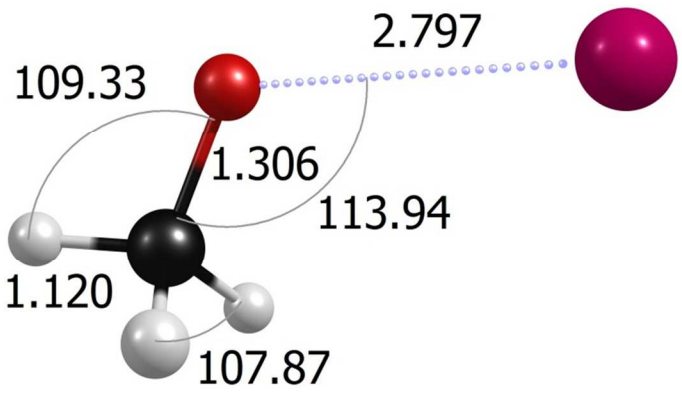

Figure S18. The optimized geometry of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 3) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms. Bond lengths (red) are in Ångstroms. Bond angles (black) are in degrees.

The normal mode frequencies (unscaled) and intensities (km/mol) of triplet methoxy cation with argon ($^3CH_3O^+$-Ar 3) calculated at the DFT/B3LYP level of theory using Gaussian 03. The cc-pVTZ basis set was used for all atoms.

60.7 (0.0), 84.0 (41.6), 135.9 (8.0), 846.7 (8.8), 906.7 (19.1), 1161.9 (70.6), 1167.6 (56.3), 1183.1 (179.7), 1266.8 (113.8), 2724.8 (360.9), 2740.9 (120.2), 2776.5 (176.5)

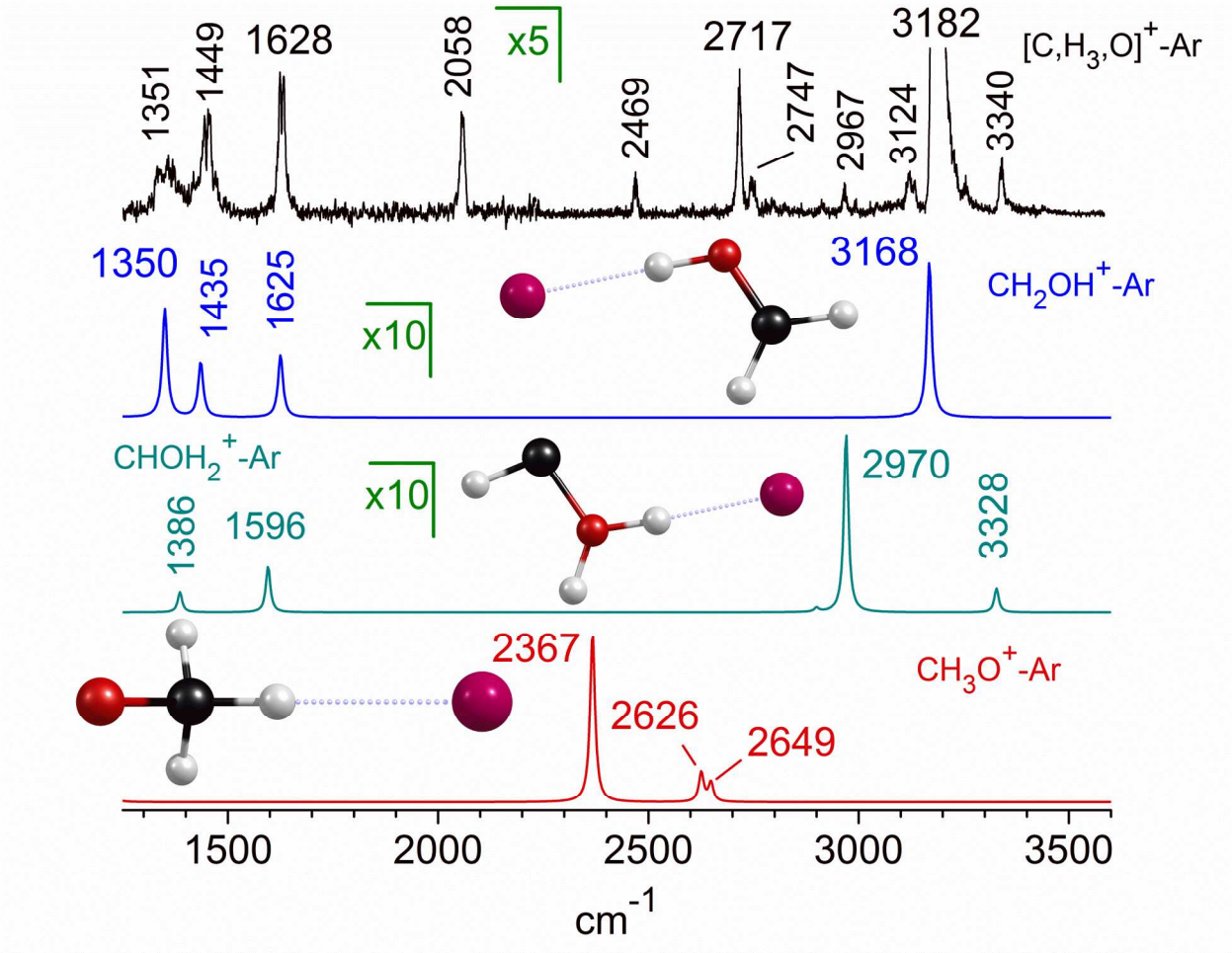

Figure S19. Comparison of the IR-PD spectrum of the mass 31 cation with argon (top trace) with vibrational frequencies (scaled) of three structural isomers computed at the DFT/B3LYP level of theory. Relative energies are available in Table S2.

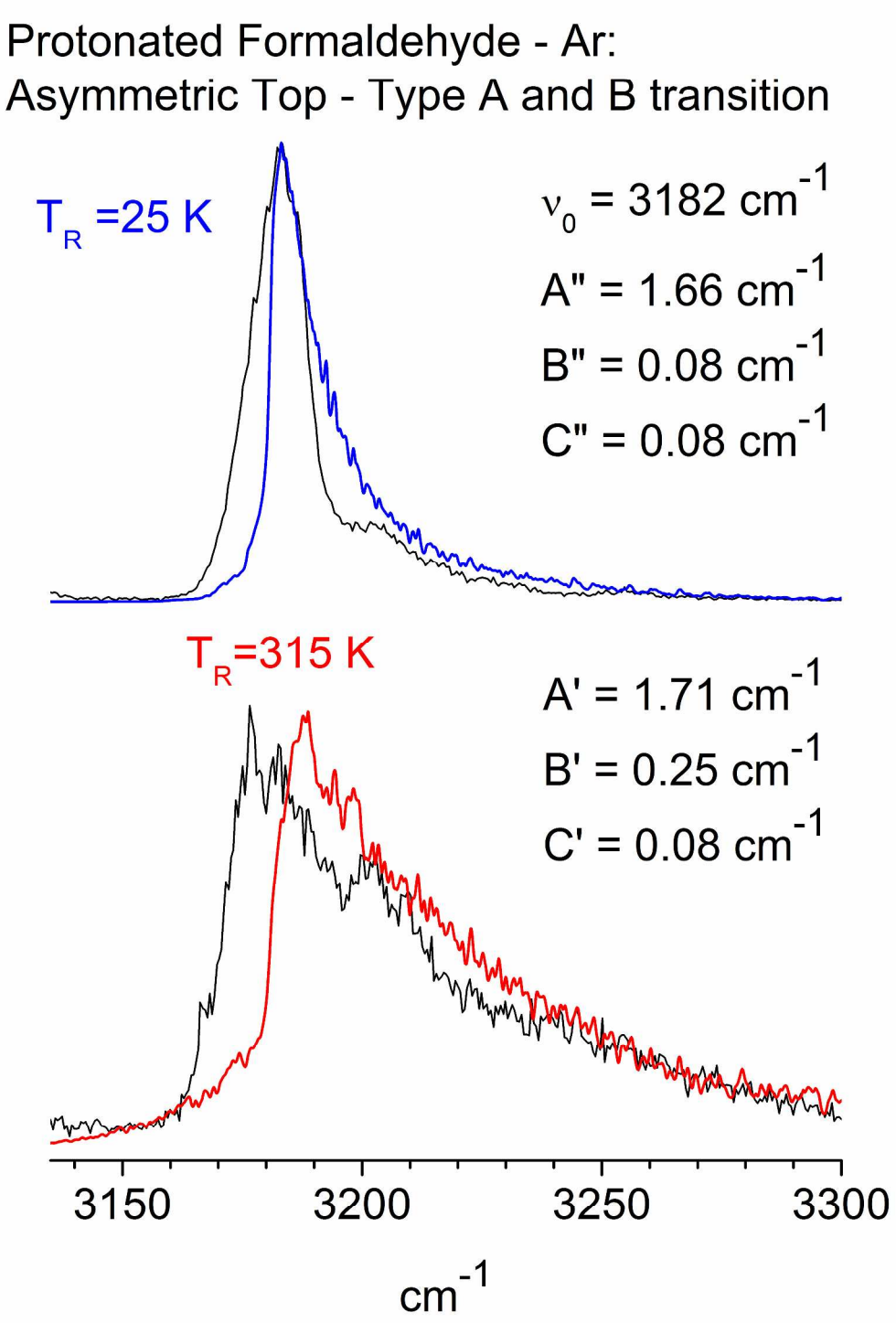

Figure S20. Comparison of the observed O–H stretch of CH_2OH^+-Ar (black) at two different source conditions with simulated ro-vibrational spectra for an asymmetric top using the PGOPHER program.

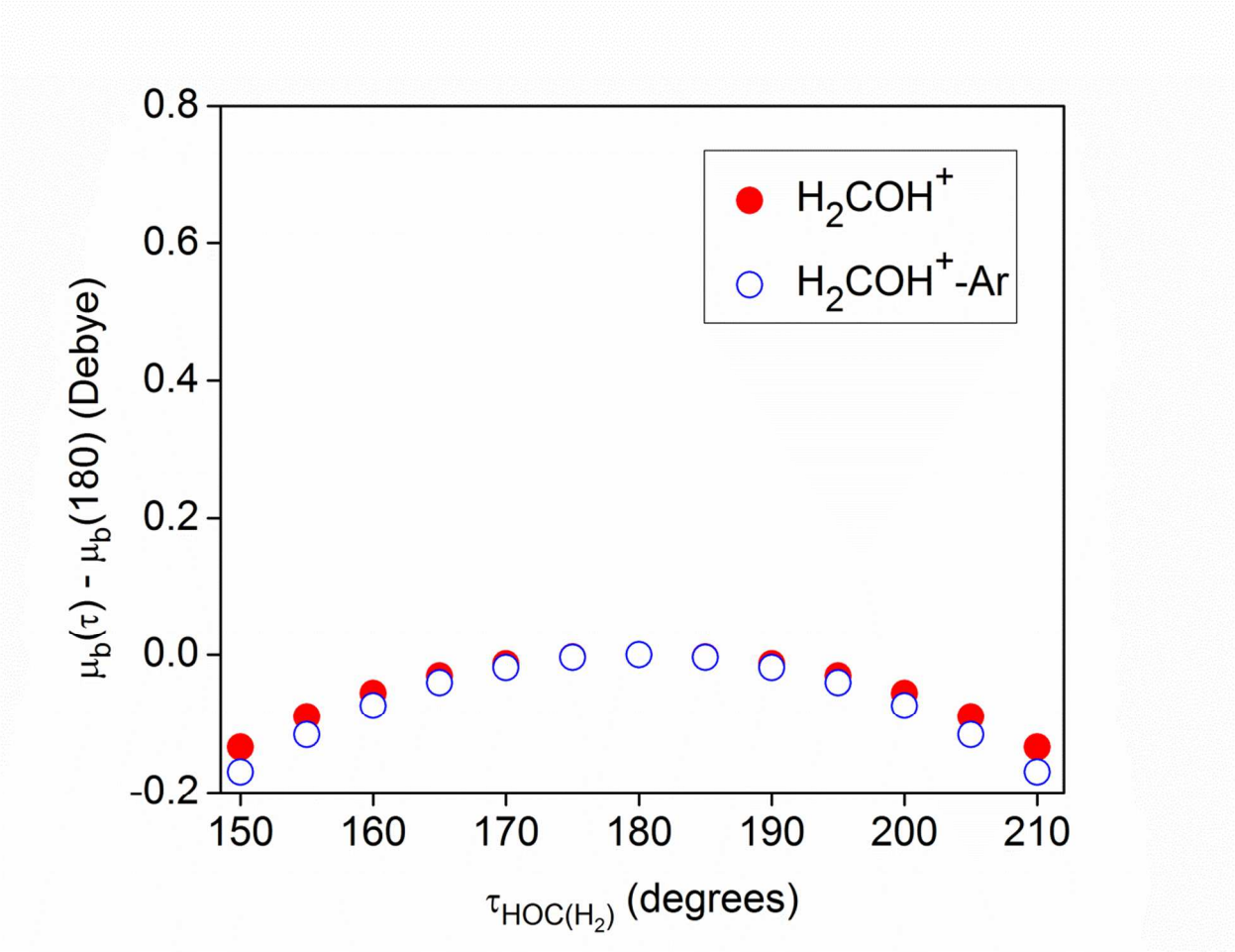

Figure S21. The variation in the component of the dipole moment along the *b*-axis, plotted as a function of the HOC(H_2) torsion angle (τ). The blue open circles are for the complex with argon present, while the red solid ones are for the complex without argon.

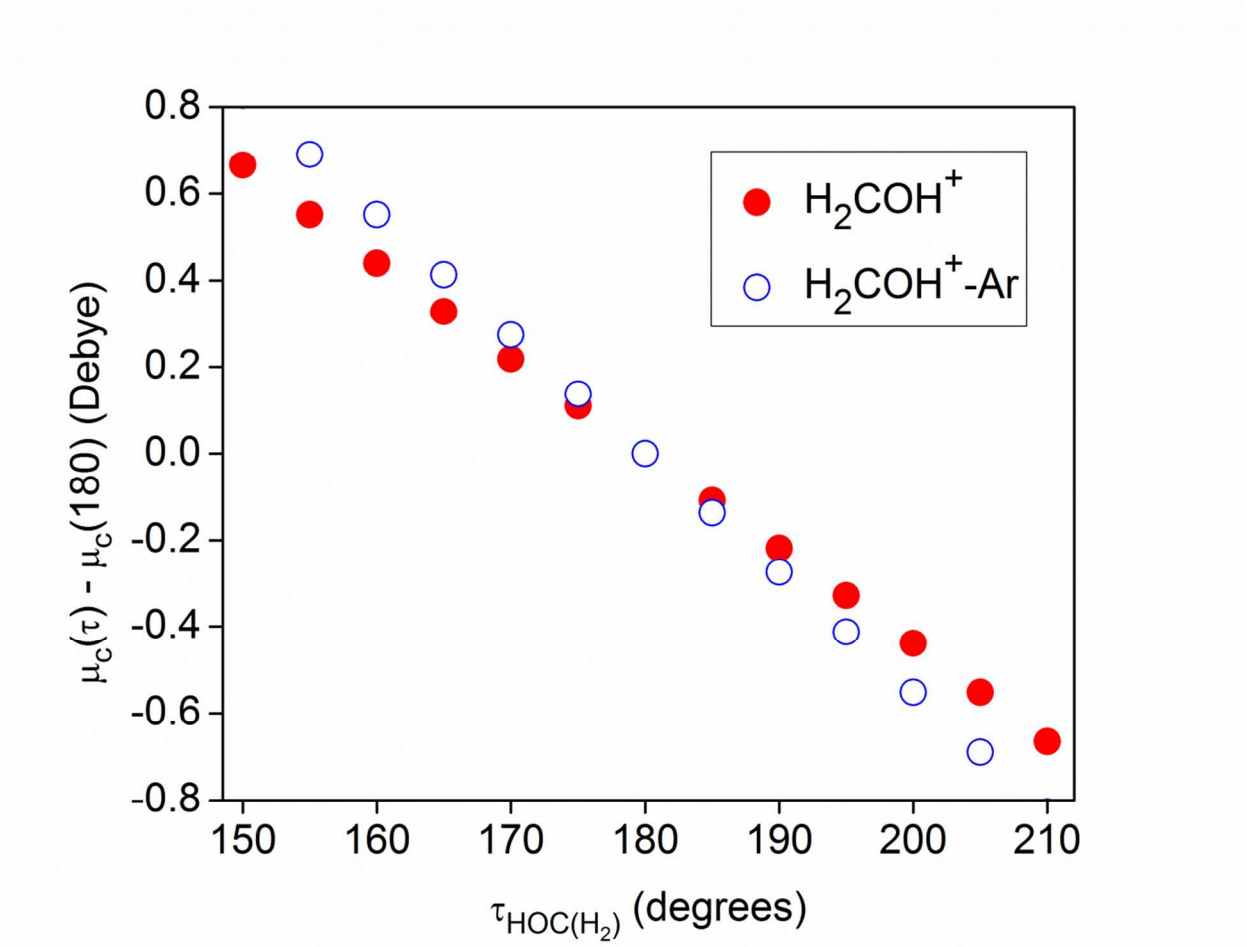

Figure S22. The variation in the component of the dipole moment along the *c*-axis, plotted -as a function of the HOC(H_2) torsion angle (τ). The blue open circles are for the complex with argon present, while the red solid ones are for the complex without argon.

Analysis of the combination band at 3340 cm^{-1}

We follow an approach that is similar to the one taken by Myshakin et al in their analysis of complexes of $CH_3NO_2^-$ and $CH_3CO_2^-$ with H_2O [J. Chem. Phys. **2003**, *119*, 10138]. In the present analysis, the Hamiltonian is reduced to the two normal coordinates, which are treated in the harmonic approximation. The two chosen coordinates are the OH stretch (q_1) and the Ar-H stretch (q_{11}). The one anharmonic term that is included is the cubic coupling term of the form ½ $f_3 q_1^2 q_{11}$, and the value of all the constants are obtained from a calculation at the MP2/6-311++G(d,p) level of theory/basis, as implemented in Gaussian. This gives a Hamiltonian of the form

$$H = \frac{p_1^2}{2} + \frac{p_{11}^2}{2} + \frac{\omega_1^2}{2} q_1^2 + \frac{\omega_{11}^2}{2} q_{11}^2 + \frac{f_3}{2} q_1^2 q_{11}.$$

In the present analysis, the energies and wave functions are obtained by employing an adiabatic approximation in which the OH stretch is treated as the high frequency mode and the eigenvalues and eigenvectors of the Hamiltonian

$$h_1(q_{11}) = \frac{p_1^2}{2} + \left(\frac{\omega_1^2}{2} + \frac{f_3}{2} q_{11} \right) q_1^2$$

are evaluated as functions of q_{11}. This yields expressions for the energies of

$$\begin{aligned} E_{n_1}(q_{11}) &= \hbar \sqrt{\omega_1^2 + f_3 q_{11}} \left(n_1 + \frac{1}{2} \right) \\ &\approx \hbar \omega_1 \left(1 + \frac{f_3}{2\omega_1^2} q_{11} \right) \left(n_1 + \frac{1}{2} \right) \end{aligned}$$

The above approximation is introduced to make the problem analytically solvable, but solving the problem numerically without invoking the approximation yields essentially the same results.

In the second step, we solve for the eigenvalues of h_{11}:

$$\begin{aligned} h_{11;n_1} &= \frac{p_{11}^2}{2} + \frac{\omega_{11}^2}{2} q_{11}^2 + \frac{\hbar f_3}{2\omega_1} \left(n_1 + \frac{1}{2} \right) q_{11} + \hbar \omega_1 \left(n_1 + \frac{1}{2} \right) \\ &= \frac{p_{11}^2}{2} + \frac{\omega_{11}^2}{2} \left(q_{11} + \frac{\hbar f_3}{2\omega_1 \omega_{11}^2} \left(n_1 + \frac{1}{2} \right) \right)^2 - \frac{\hbar^2 f_3^2}{8\omega_1^2 \omega_{11}^2} \left(n_1 + \frac{1}{2} \right)^2 + \hbar \omega_1 \left(n_1 + \frac{1}{2} \right) \end{aligned}$$

which yields

$$E_{n_1, n_{11}} = \hbar \omega_1 \left(n_1 + \frac{1}{2} \right) + \hbar \omega_{11} \left(n_{11} + \frac{1}{2} \right) - \frac{\hbar^2 f_3^2}{8\omega_1^2 \omega_{11}^2} \left(n_1 + \frac{1}{2} \right)^2$$

Here the corresponding wave functions are harmonic oscillators, and they are centered around

$$q_{11}^{\min}(n_1) = -\frac{\hbar f_3}{2\omega_1 \omega_{11}^2}\left(n_1 + \frac{1}{2}\right)$$

rather than q_{11}=0.

The overlap of shifted harmonic oscillator eigenstates are well-known, and within a Franck-Condon treatment the intensities of combination bands involving one quantum of excitation in the OH stretch and n_{11} quanta in the Ar-H stretch rae given by

$$I_{n_{11}} = \frac{e^{-\Delta q_{11}^2/2}\left(\Delta q_{11}\right)^{2n_{11}}}{2^{n_{11}} n_{11}!}$$

where (in dimensionless coordinates)

$$\Delta q_{11}(n_1) = -\frac{\hbar f_3 n_1 \sqrt{\omega_{11}}}{2\omega_1 \omega_{11}^2} = -\frac{\tilde{F}_3 n_1}{2\tilde{\omega}_{11}}$$

Using the values from the electronic structure calculations, $\tilde{\omega}_1 = 3503$ cm^{-1}, $\tilde{\omega}_{11} = 130.6$ cm^{-1}, and $\tilde{F}_3 = 72.79$ cm^{-1} leads to the prediction that the fundamental of the OH stretch gets 96.2% of the integrated intensity while the remaining 3.8% would go to the combination band involving one quantum in each mode.