

Electron Affinities, Well Depths, and Vibrational Spectroscopy of *cis*- and *trans*-HOCO

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 Supporting Information

ABSTRACT: We report vibrationally resolved photoelectron spectra of internally cold HOCO[−] and DOCO[−] anions at wavelengths near and well above the detachment threshold. These spectra are dominated by a strong Franck–Condon progression of three low-energy modes of the *cis* isomer, the first gas-phase measurement of these vibrations. Using highly resolved, near-threshold spectra we are able to reassign the electron affinities (EAs) of *cis*- and *trans*-HOCO to 1.51 ± 0.01 and 1.37 ± 0.01 eV, respectively. Using these EAs, well depths with respect to OH + CO are determined to be 1.07 ± 0.02 eV for *trans*-HOCO and 0.99 ± 0.02 eV for *cis*-HOCO. High-level *ab initio* calculations show excellent agreement with all experimental results. These values will be of direct use in thermochemical calculations and will help to aid in the identification of the HOCO radical in complex reactions.

The reaction OH + CO → H + CO₂ and its intermediate species, the HOCO radical, have garnered a significant amount of attention over the past several decades due to its importance in atmospheric¹ and combustion processes,² but significant gaps still exist in the understanding of the detailed mechanism of this reaction. The HOCO radical has proven relatively difficult to isolate, limiting the range of techniques brought to bear upon it, and thus it remains poorly characterized. It is believed that the HOCO intermediate can be stabilized by a third body, opening the potential for significant radical chemistry,³ and a more thorough understanding of the isolated radical is necessary to evaluate the role these types of interactions may play in bulk processes. Matrix isolation studies in CO, neon, and argon have identified most of the fundamental frequencies of the *cis* and *trans* isomers of both HOCO and DOCO,^{4–6} but gas-phase experiments have been limited to direct absorption measurements of the OH^{7–9} and terminal CO¹⁰ stretching modes of *trans*-HOCO. Displacement vectors for the vibrational modes for both isomers are provided as Supporting Information. Rotational spectra of *cis*-¹¹ and *trans*-HOCO^{11–13} are consistent with *ab initio* structures.¹⁴ Electron affinities (EAs) for both isomers have been calculated and found to be in rough agreement with dissociative photodetachment results,^{15,16} though the isomeric composition in those experiments was unknown. Photoelectron spectra near threshold (772 nm) revealed two peaks at

low electron kinetic energy that were not conclusively assigned, as a broad background arising from internally excited anions prevented unambiguous resolution of the peaks.¹⁷ These features were recently suggested to arise from vibrational Feshbach resonances in dipole-bound states, though the potential for pure photodetachment was not ruled out.¹⁸

Here we report a systematic photoelectron imaging study of HOCO and DOCO by detachment of vibrationally cold HOCO[−] and DOCO[−] anions. Photoelectron spectra with well-resolved vibrational structure are presented and compared to high-level calculations. The data yield revised EAs along with the first gas-phase frequencies of several vibrational modes of *cis*- and *trans*-HOCO and DOCO. Given these EAs, the well depths for both isomers are calculated, making use of previously reported dissociative photodetachment results.¹⁹

Figures 1 and 2 show photoelectron spectra for HOCO[−] and DOCO[−] at 660 (1.878 ± 0.002 eV) and 775 nm (1.601 ± 0.002 eV), respectively. A phenomenological fit, guided by Franck–Condon simulations, of the experimental ν_3 , ν_4 , and ν_5 frequencies of *cis* and *trans* isomers to both spectra is also shown. Calibration to spin–orbit splitting in O[−] photodetachment at 775 nm yields an instrumental resolution of 0.014 at 0.14 eV; that at 660 nm yields an instrumental resolution of 0.020 at 0.42 eV. Also included are the photoelectron angular distributions (PADs) at both wavelengths, characterized by optimizing the anisotropy parameter β in the equation $I(\theta) \propto 1 + \beta P_2(\cos \theta)$ to the measured PAD at a given energy. The fitted vibrational frequencies for the above modes are given in Table 1, which also summarizes existing vibrational data from gas-phase and matrix isolation studies as well as the current *ab initio* calculations of the vibrational energies. Uncertainties in the measured frequencies are ± 5 cm^{−1} for ν_5 and ± 10 cm^{−1} for ν_3 and ν_4 .

The adiabatic EAs are determined directly from the *cis* and *trans* origins for HOCO and DOCO in the 775 nm spectra. For *cis*- and *trans*-HOCO these are 1.51 ± 0.01 and 1.38 ± 0.01 eV, respectively, with EAs of 1.501 and 1.373 eV computed using the HEAT345-(Q) protocol (see below) showing better than 100 cm^{−1} agreement, within experimental errors. For the DOCO case, measured EAs are 1.51 ± 0.01 and 1.37 ± 0.01 eV, again in good agreement with the calculated DOCO EAs of 1.501 and 1.371 eV, respectively. These assignments of the higher-energy

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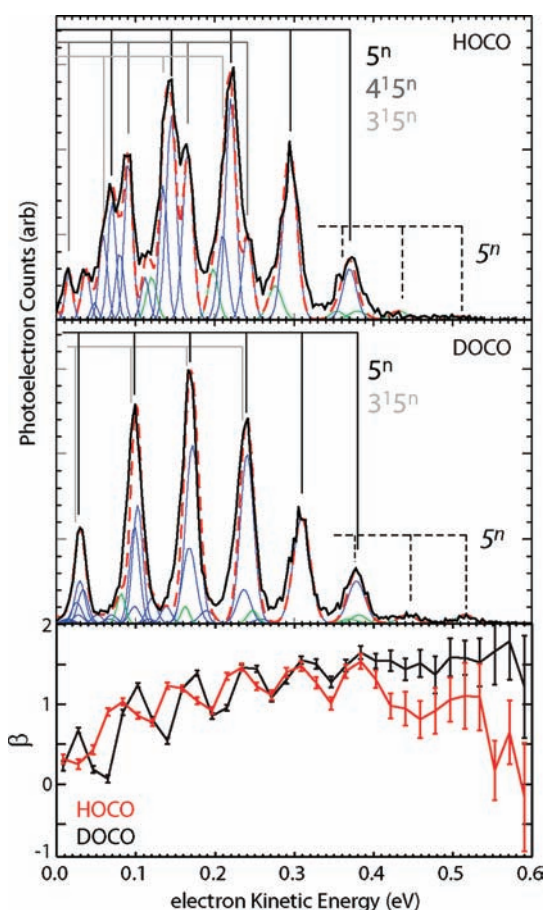


Figure 1. Photoelectron spectra of HOCO and DOCO at 660 nm (black) with fits (dashed red) from the extracted *cis* (blue) and *trans* (green) frequencies. Extracted photoelectron anisotropy parameters for HOCO and DOCO are shown in the bottom panel. Solid (dashed) combs denote dominant *cis* (*trans*) transitions. In each comb the right-most line denotes $n = 0$.

peaks to *trans*-HOCO rather than hot bands is further supported by the measured PADs at 775 nm, which show a small drop in anisotropy between the second and third peaks from what would be expected due to threshold effects,²⁰ consistent with photodetachment from a slightly different molecular configuration. This anisotropy change is also seen in the 660 nm PADs beyond the *cis* origin.

With the EAs established, fits to the 660 and 775 nm spectra simultaneously are obtained from harmonic combinations of ν_3 , ν_4 , and ν_5 in both isomers. These fits are composed of Gaussian-convolved peaks with variable fundamental frequencies and intensities, and widths given by the phenomenologically determined instrument resolution $0.028\text{eKE} + 0.010\text{ eV fwhm}$. The 660 nm HOCO spectrum is dominated by three primary sequences, the 5^n , $4^1 5^n$, and $3^1 5^n$ combination modes of the *cis* isomer. No vibrational excitation of ν_2 is resolved, with minimal excitation predicted in Franck–Condon simulations. The ν_1 mode is not energetically accessible at either wavelength, and it is also not predicted to have significant excitation. The anion and neutral structures of both isomers are planar, so no excitation in ν_6 is expected or seen. The 5^1 band of the *trans* isomer is also resolved, though all other features from this isomer are obscured by the signal from the dominant *cis* isomer. Interestingly, in the

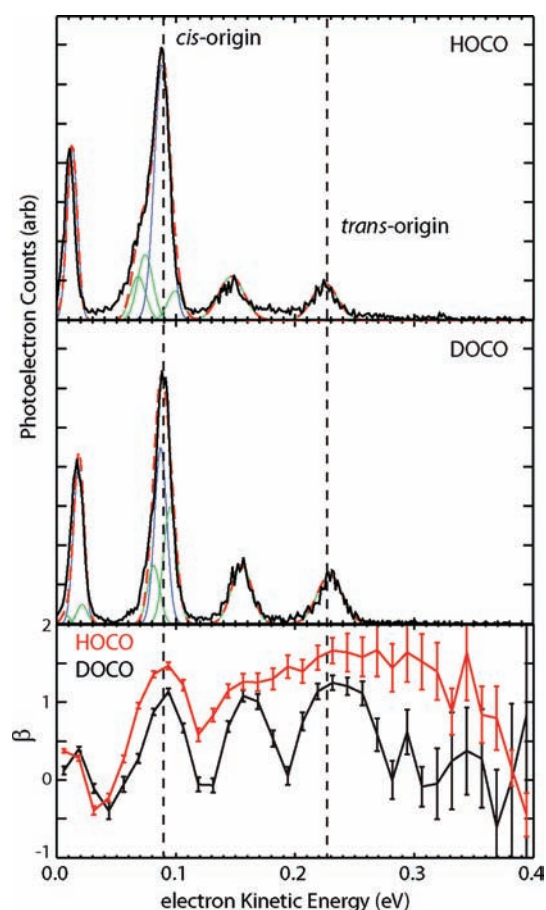


Figure 2. Same as Figure 1 for 775 nm photons.

case of DOCO, the three primary sequences show a significant degree of overlap, and the ν_4 mode is neither observed nor predicted in *cis*- or *trans*-DOCO. Although individual transitions are not resolved in the DOCO spectrum, these spectral features are broader than the instrumental resolution, and thus the frequencies can be extracted using the same fitting procedure described above. For example, the peak at 0.1 eV in the 660 nm *cis*-HOCO spectrum is composed of 5^5 and $3^1 5^3$ contributions, which when fit provide a reasonable estimate of ν_3 and ν_5 .

In order to better resolve the *trans*-HOCO modes, the 775 nm spectra were decomposed into appropriate contributions from *cis* and *trans* isomers, and the peak heights and locations were optimized to best reproduce the shape of the feature centered around 0.09 eV. Though this peak is primarily composed of the *cis*-HOCO origin, the low-energy shoulder was found to contain contributions from *trans*-HOCO 5^2 and 3^1 as well, allowing for more precise determination of ν_3 . The high-energy side of the feature includes the 4^1 mode. Because this feature narrows significantly in the DOCO spectrum, the above analysis is more difficult in this case, and the ν_4 frequency could not be reliably determined for DOCO.

Interestingly, the origin and 5^1 bands of *trans*-HOCO in the 775 nm spectrum are found to be broader ($\sim 0.025\text{ eV}$) than the instrument resolution at these electron kinetic energies. The reason for this is not currently clear, as the spectra appear to be primarily a result of direct photodetachment, but the potential for broad dipole-supported resonances as outlined by Miyabe et al. cannot be ruled out.¹⁸ It is also possible that the ion formation

Table 1. Vibrational Frequencies for HOCO and DOCO from Past Experiments and This Work

mode	description	this expt	past expt ^a	harmonic	anharmonic
<i>cis</i> -HOCO (DOCO)					
ν_1	OH stretch		3316 ⁴	3667 (2666)	3458 (2555)
ν_2	CO stretch		1797 ⁴	1852 (1851)	1815 (1814)
ν_3	HOC bend	1290 (1145)	1261 ⁴	1313 (1155)	1282 (1121)
ν_4	OC stretch	1040	1088 ⁴	1076 (978)	1042 (949)
ν_5	OCO bend	605 (557)	620 ⁴	602 (543)	596 (535)
ν_6	torsion			578 (476)	545 (454)
<i>trans</i> -HOCO (DOCO)					
ν_1	OH stretch		3636 ⁷ (2684 ⁹)–3628 ⁶ (2678 ⁶)	3830 (2788)	3641 (2688)
ν_2	CO stretch		1853 ¹⁰ (1852 ¹⁰)–1848 ⁶ (1846 ⁶)	1895 (1884)	1854 (1845)
ν_3	HOC bend	1194 (1081)	1210 ⁶ (1083 ⁶)	1258 (1119)	1217 (1081)
ν_4	OC stretch	1048	1050 ⁶	1086 (924)	1057 (900)
ν_5	OCO bend	629 (597)	615 ⁴	621 (594)	614 (588)
ν_6	torsion		508 ⁶	536 (411)	507 (395)

^a Italicized values represent gas-phase measurements. All other values are matrix isolation measurements. Sources are cited as superscript numbers.

mechanism, thought to be addition of OH⁻ to CO, induces a larger rotational temperature for the *trans* isomer than of the *cis* isomer, yielding peaks that are rotationally broadened. Given a rotational constant of ~ 4 cm⁻¹, rotational temperatures of 140 K reproduce the observed broadening. While no evidence of vibrational hot bands exists in the spectra, inefficient rotation–vibration coupling could lead to a long-lived nonstatistical distribution of energy between vibrational and rotational degrees of freedom in the anion. This mechanism could yield sequence bands, which may also contribute to peak broadening. No power dependence was observed over a range of power densities from 2×10^{10} to 2×10^9 W/cm².

It is possible to estimate the relative populations of the two isomers in the ion beam by scaling the Franck–Condon simulated spectra of each isomer to fit the data. This method does not take into account the electronic transition cross sections, but they are expected to be similar due to the high degree of similarity between the HOMOs of the two isomers.¹¹ Computed Franck–Condon factors (FCFs) are scaled by a function approximating the Wigner threshold law, implemented here as $a + b\text{eKE}^{0.5} + c\text{eKE}^{1.5}$, where $\{a, b, c\} = \{0.005, 0.1, 1.0\}$. The spectrum is then simulated by a summation of Gaussian peaks with centers at the calculated peak positions, widths as described above, and amplitudes set so that the peak area equals the corresponding FCF. The simulated spectrum for each isomer is scaled to produce a best fit to the measured spectrum, and the ratio of the scaling factors gives the contribution of each isomer to the overall spectrum. The best-fit *trans*-HOCO fractions range from 3 to 5%, and for *trans*-DOCO from 5 to 7%, depending on the wavelength. The noted ranges arise primarily from difficulties in accurately accounting for threshold effects.²⁰

Finally, by comparing these EAs with recent dissociative photodetachment studies of HOCO⁻ which found a maximum total energy release ($E_{\text{tot}} = \text{eKE} + \text{fragment translational energy}$) of 0.70 eV for OH + CO dissociation,¹⁹ the well depths of the *cis* and *trans* isomers can be determined quite accurately. These well depths vary by more than 0.3 eV among the various high-level surfaces developed in the past decade.^{21–24} Given the assumption that the beam is essentially entirely *cis*-HOCO, the well depth as referenced to the OH + CO asymptotic energy can be

determined by $D_0 = h\nu - E_{\text{tot}} - \text{EA}$, and the *trans* well can be estimated using the absolute difference in energy calculated for the *cis*- and *trans*-HOCO wells. This calculation gives well depths of 0.99 ± 0.02 and 1.07 ± 0.02 eV for the *cis* and *trans* isomers, respectively, within the upper limit of 1.25 eV set by photoionization experiments on *trans*-HOCO²⁵ and in the range of values calculated in the existing full surfaces. These errors are primarily due to uncertainty in the relative contributions of the instrument resolution and the product rotational distribution for the coincidence data in ref 19. The HEAT345-(Q) values for the well depths, which are available by combining the calculations here with those in ref 32, are 1.01 and 1.08 eV, respectively, in good agreement with the experimental values and with an expected error of ± 0.01 eV. If the OH + CO signal originates from *trans*-HOCO⁻, then these well depths are revised to 1.07 and 1.13 eV, respectively, with the same error, inconsistent with the calculated values.

The photoelectron imaging studies were carried out in the cryogenic ion-trap photoelectron–photofragment coincidence spectrometer described in previous dissociative photodetachment studies of the OH + CO reaction.¹⁹ HOCO⁻ (DOCO⁻) anions were generated in a 10 Hz pulsed supersonic expansion of a 6% CO, 6% CH₄ (CD₄), 13% N₂O, 75% Ar gas mix through a pulsed coaxial discharge and crossed by a 1 keV electron beam. Ions were accelerated to 5 or 7 keV, mass-selected by time-of-flight, and stored in a cryogenic electrostatic ion beam trap for periods of 100 ms to 1 s. While trapped, ions were bunched and synchronized to a 1 kHz, 775 nm Ti:sapphire amplifier and optical parametric amplifier (TOPAS) system providing <2 ps pulses at the fundamental and at 660 nm. Photoelectron spectra at both wavelengths were recorded using a velocity-map-imaging time- and position-sensitive photoelectron detector. Wavelengths were measured using a fiber-optic spectrometer calibrated to a helium–neon discharge emission spectrum covering the 600–750 nm range.

Vibrational frequencies were calculated using analytic second-derivative techniques at the CCSD(T) level of theory,^{26–28} in conjunction with second-order vibrational perturbation theory (VPT2).²⁹ These *ab initio* calculations, which were done in the frozen-core approximation, used the atomic natural orbital

(ANO) basis sets of Almlöf and Taylor.³⁰ The anharmonic frequencies (as well as the anharmonicity constants) were calculated using the 4s2p1d (on H) and 4s3p2d1f (other atoms) truncation known as ANO1, while the harmonic frequencies were determined with the ANO2 basis set, which is contracted as 4s3p2d1f (H) and 5s4p3d2f1g (other atoms). The values given in Table 1 are the harmonic levels from the ANO2 calculations and the VPT2 results, obtained by using the ANO2 harmonic force field together with the ANO1 cubic and quartic force constants. The calculated frequencies are found to match very well with detailed calculations for *trans*-HOCO published during the preparation of this manuscript.³¹

Electron affinities of both isomers were calculated using the high-accuracy extrapolated *ab initio* thermochemistry (HEAT)³² protocol known as HEAT345-(Q).^{33,34} In this work, however, the zero-point vibrational correction to the energies of all species involved (both conformers and their anions) were obtained at the CCSD(T)/ANO1 level, instead of the CCSD(T)/cc-PVQZ level which is the standard approach. All calculations done here were carried out with the CFOUR quantum chemistry package.³⁵

■ ASSOCIATED CONTENT

S **Supporting Information.** Vibrational mode displacement vectors for *cis*- and *trans*-HOCO, Franck–Condon stick spectra for both wavelengths, and complete ref 35. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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