# Supplementary Information

## A $1 + 1'$ resonance-enhanced multiphoton ionization scheme for rotationally state-selective detection of formaldehyde via the $\tilde{\mathrm{A}}\,^1\mathrm{A}_2 \leftarrow \tilde{\mathrm{X}}\,^1\mathrm{A}_1$ transition

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## S.I. ABSOLUTE SIGNAL COMPARISON TO A BENCHMARK SYSTEM

In order to provide an estimate of the absolute sensitivity of our REMPI scheme, we performed a back-to-back signal comparison with the well characterized $1 + 1$ REMPI signal of the NO molecule via the $\mathrm{A}^2\Sigma^+$, $v' = 0 \leftarrow \mathrm{X}^2\Pi$, $v'' = 0$ transition. We use the $\mathrm{Q}_{11}(0.5)$ rotational line of the NO transition at 225.25 nm to compare with the $\tilde{\mathrm{A}} \leftarrow \tilde{\mathrm{X}}\ 4^1_0\ J_{K_aK_c} = 1_{01} \leftarrow 1_{11}$ rotational line of formaldehyde at 353.30 nm.

For the NO measurement, we used a gas mixture of 1.2% NO in $\mathrm{H}_2$, with a nozzle backing pressure of 12 bar. For the formaldehyde measurement, we also backed the nozzle with 12 bar of $\mathrm{H}_2$. We measured the relative number density of NO and formaldehyde in the molecular beams used in the two experiments by comparing the relative signals on a residual gas analyzer (SRS RGA200) in the UHV detection chamber. We adjusted the paraformaldehyde cracking temperature until the signals were equal, after correcting for the relative electron impact ionization cross sections at 70 eV (2.8 and 4.1 Å$^2$, respectively, for NO and formaldehyde). In both experiments, we determine the rotational temperature in the molecular beam from the measured rotational population distribution. For NO, we obtain a rotational temperature of 13 K, and 42% population in the $J'' = 0.5$ ground state. For formaldehyde, we obtain a 6.5 K rotational temperature (for the ortho and para manifolds, individually), which indicates a population of 14% in the $M_J = \pm 1$ sublevels of the $J''_{K''_aK''_c} = 1_{11}$ level (the $M_J = 0$ sublevel contributes no intensity to the Q-branch transition in question). For NO, we used a 225 nm laser fluence of 15 J/m$^2$, and for formaldehyde, we use a 157 nm fluence of 545 J/m$^2$. Both experiments are performed in a regime in which the first, resonant transition is saturated.

In both experiments, we scanned the timing of the nozzle trigger in order to integrate the absolute ion signal over the molecular beam pulse. We obtain a relative integrated ion signal of 1:1.07 for NO:formaldehyde. This indicates a sensitivity factor of $\sim$11:1 per unit state-specific population per unit ionization laser fluence. This result suggests that the sensitivity of our $1 + 1'$ formaldehyde REMPI scheme is on a similar order of magnitude to that of the $1 + 1$ NO REMPI scheme. However, due to uncertainty in the laser beam profiles used in our comparison (which we estimate by comparing burn spots), this result is reliable to no better than one order of magnitude. Furthermore, when employing looser focussing conditions, we have observed depletion of the MCP sensitivity that occurs as a result of scatter of 157 nm VUV radiation. Therefore, it is uncertain whether the relative detection efficiency of formaldehyde is due exclusively to the value of the photoionization cross section relative to the $(7.0 \pm 0.9) \times 10^{-19}$ cm$^2$ ionization cross section of the $\mathrm{A}^2\Sigma^+$, $v' = 0$ state of NO,[1] or whether it includes other experimental factors as well. Finally, the comparison does not take into account background non-resonant multiphoton ionization which depends on the 157 nm focussing conditions and can limit the observable signal-to-noise ratio. The spectra shown in the current work were obtained in a regime where such background was negligible ($<1\%$ of the resonant signal).

## S.II. TABULATION OF INTENSITIES FROM A ROTATIONALLY COLD SPECTRUM

Table S.I provides a list of observed integrated line intensities ($S_{\mathrm{obs}}$) in the $T_{\mathrm{rot}} = 8$ K $1+1'$ REMPI spectrum of the $\tilde{\mathrm{A}} \leftarrow \tilde{\mathrm{X}}$ ($4^1_0$) transition shown in Fig. 4 of our paper, which are used to generate the Boltzmann plot shown in Fig. 5. The transitions are labeled using the notation, ${}^{\Delta K_a,\Delta K_c}\Delta J_{K''_a,K''_c}(J'')$. The calculated normalized intensities ($S_{\mathrm{cal}}$) are shown for comparison and the percent error, $[(S_{\mathrm{obs}} - S_{\mathrm{cal}})/S_{\mathrm{cal}})] \times 100\%$, is tabulated. The average absolute error is 26.0%.

[1] H. Zacharias, R. Schmiedl, and K. H. Welge. State selective step-wise photoionization of NO with mass spectroscopic ion detection. *Applied physics*, 21(2):127–133, 1980.

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TABLE S.I. The observed list of frequencies and normalized integrated line intensities ($S_{\mathrm{obs}}$) from the $T_{\mathrm{rot}} = 8$ K $1+1'$ REMPI spectrum of the $\tilde{\mathrm{A}} \leftarrow \tilde{\mathrm{X}}$ ($4_0^1$) transition shown in Fig. 4 of our paper. The calculated normalized intensities ($S_{\mathrm{cal}}$) and percent error are also tabulated.

| Transition | $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | Freq. (cm$^{-1}$) | $S_{\mathrm{obs}}$ | $S_{\mathrm{calc}}$ | % error |
|---|---|---|---|---|---|---|---|---|---|---|
| ${}^{\mathrm{p,p}}\mathrm{P}_{1,1}(1)$ | 0 | 0 | 0 | 1 | 1 | 1 | 28302.02 | unresolved | | |
| ${}^{\mathrm{p,p}}\mathrm{P}_{1,2}(2)$ | 1 | 0 | 1 | 2 | 1 | 2 | 28299.46 | 0.0550 | 0.0502 | 9.57 |
| ${}^{\mathrm{p,p}}\mathrm{P}_{1,3}(3)$ | 2 | 0 | 2 | 3 | 1 | 3 | 28296.69 | 0.0201 | 0.0189 | 6.44 |
| ${}^{\mathrm{p,p}}\mathrm{P}_{1,4}(4)$ | 3 | 0 | 3 | 4 | 1 | 4 | 28293.70 | 0.00833 | 0.00440 | 89.19 |
| ${}^{\mathrm{p,r}}\mathrm{Q}_{1,0}(1)$ | 1 | 0 | 1 | 1 | 1 | 0 | 28304.00 | 0.148 | 0.114 | 30.72 |
| ${}^{\mathrm{p,r}}\mathrm{Q}_{1,1}(2)$ | 2 | 0 | 2 | 2 | 1 | 1 | 28303.25 | 0.0712 | 0.0761 | −6.55 |
| ${}^{\mathrm{p,r}}\mathrm{Q}_{1,2}(3)$ | 3 | 0 | 3 | 3 | 1 | 2 | 28302.12 | unresolved | | |
| ${}^{\mathrm{p,r}}\mathrm{Q}_{1,3}(4)$ | 4 | 0 | 4 | 4 | 1 | 3 | 28300.62 | 0.00660 | 0.00567 | 16.32 |
| ${}^{\mathrm{p,r}}\mathrm{R}_{1,1}(1)$ | 2 | 0 | 2 | 1 | 1 | 1 | 28308.43 | 0.0800 | 0.0398 | 100.94 |
| ${}^{\mathrm{p,r}}\mathrm{R}_{1,2}(2)$ | 3 | 0 | 3 | 2 | 1 | 2 | 28310.14 | 0.0339 | 0.0347 | −2.37 |
| ${}^{\mathrm{p,r}}\mathrm{R}_{1,3}(3)$ | 4 | 0 | 4 | 3 | 1 | 3 | 28311.62 | 0.0156 | 0.0149 | 4.30 |
| ${}^{\mathrm{p,r}}\mathrm{R}_{1,4}(4)$ | 5 | 0 | 5 | 4 | 1 | 4 | 28312.89 | 0.00480 | 0.00375 | 27.94 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{1,2}(2)$ | 2 | 2 | 1 | 2 | 1 | 2 | 28334.46 | 0.0233 | 0.0279 | −16.29 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{1,1}(2)$ | 2 | 2 | 0 | 2 | 1 | 1 | 28333.98 | unresolved | | |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{1,3}(3)$ | 3 | 2 | 2 | 3 | 1 | 3 | 28333.82 | unresolved | | |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{1,2}(3)$ | 3 | 2 | 1 | 3 | 1 | 2 | 28332.86 | 0.0105 | 0.0120 | −12.54 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{1,0}(1)$ | 2 | 2 | 1 | 1 | 1 | 0 | 28339.00 | 0.125 | 0.114 | 10.05 |
| ${}^{\mathrm{r,p}}\mathrm{R}_{1,1}(1)$ | 2 | 2 | 0 | 1 | 1 | 1 | 28339.16 | 0.125 | 0.116 | 7.70 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{1,1}(2)$ | 3 | 2 | 2 | 2 | 1 | 1 | 28340.38 | 0.0336 | 0.0511 | −34.33 |
| ${}^{\mathrm{r,p}}\mathrm{R}_{1,2}(2)$ | 3 | 2 | 1 | 2 | 1 | 2 | 28340.87 | 0.0358 | 0.0545 | −34.41 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{1,2}(3)$ | 4 | 2 | 3 | 3 | 1 | 2 | 28341.40 | 0.00944 | 0.0149 | −36.61 |
| ${}^{\mathrm{r,p}}\mathrm{R}_{1,3}(3)$ | 4 | 2 | 2 | 3 | 1 | 3 | 28342.38 | 0.0118 | 0.0169 | −30.10 |
| ${}^{\mathrm{r,p}}\mathrm{R}_{1,4}(4)$ | 5 | 2 | 3 | 4 | 1 | 4 | 28343.69 | 0.00420 | 0.00341 | 23.15 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{1,3}(4)$ | 5 | 2 | 4 | 4 | 1 | 3 | 28342.04 | unresolved | | |
| ${}^{\mathrm{r,p}}\mathrm{P}_{0,2}(2)$ | 1 | 1 | 1 | 2 | 0 | 2 | 28315.04 | 0.00974 | 0.00876 | 11.20 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{0,1}(1)$ | 1 | 1 | 0 | 1 | 0 | 1 | 28320.01 | 0.0311 | 0.0611 | −49.19 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{0,2}(2)$ | 2 | 1 | 1 | 2 | 0 | 2 | 28319.54 | 0.0327 | 0.0421 | −22.33 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{0,3}(3)$ | 3 | 1 | 2 | 3 | 0 | 3 | 28318.84 | 0.0112 | 0.0157 | −28.89 |
| ${}^{\mathrm{r,p}}\mathrm{Q}_{0,4}(4)$ | 4 | 1 | 3 | 4 | 0 | 4 | 28317.91 | 0.00528 | 0.00346 | 52.90 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{0,0}(0)$ | 1 | 1 | 1 | 0 | 0 | 0 | 28322.32 | 0.0785 | 0.0631 | 24.50 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{0,1}(1)$ | 2 | 1 | 2 | 1 | 0 | 1 | 28324.05 | 0.0590 | 0.0611 | −3.54 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{0,2}(2)$ | 3 | 1 | 3 | 2 | 0 | 2 | 28325.43 | 0.0221 | 0.0342 | −35.37 |
| ${}^{\mathrm{r,r}}\mathrm{R}_{0,3}(3)$ | 4 | 1 | 4 | 3 | 0 | 3 | 28326.47 | 0.0116 | 0.0117 | −0.81 |
| | | | | | | | | | Average \|% error\|: | 26.0 |