Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Decomposing anharmonicity and mode-coupling from matrix effects in the IR spectra of matrix-isolated carbon dioxide and methane

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Samples used in our experiments

The used samples are $^{12}C^{16}O_2$ gas (99.9995%, Messer Austria, Order-Number=1290102114, Lot=27531923), $^{12}CH_4$ (99.995%, Methan 4.5 delivered by Messer Austria, Order-Number=108330011, Lot=140218) and $^{12}CD_4$ (99.99%, Methane D4 delivered by Euriso-top France, Order-Number=GE067L, Lot=29/032001, Cylinder-Number=8107).

Observed isotopoloques of carbon dioxide

For carbon dioxide, we observe traces of ^{13}C and ^{18}O, mainly as $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$. After PES transformation, we computed the vibrational states and intensities of these two isotopoloques with VSCF/VCI, using the same settings mentioned in the paper. The results are shown together with the main isotopoloque $^{12}C^{16}O_2$ in Table S1.

Table S1: Directly observed vibrational transitions of the CO_2 monomer.
VCI-5 / 4D CCSD(T)-F12/VTZ-F12, Gas-Reference: NIST Database

	Transition (irrep)	active	Ar	Ne	Gas	VCI	HA
$^{12}C^{16}O_2$ ($D_{\infty h}$)	**$2\nu_2 + \nu_3$** ($A_{1u} + E_{2u} = \Sigma^+_u + \Delta_u$)	IR	**3707.8** **3700.2**	**3714.7**		**3713.8**	
	$\nu_1 + \nu_3$ ($A_{1u} = \Sigma^+_u$)	IR	**3603.8** **3597.6**	**3612.4**		**3610.6**	
	ν_3 ($A_{1u} = \Sigma^+_u$)	IR	**2345.6** **2339.5**	**2348.2**	*2349.2*	**2347.4**	**2394.9**
	$2\nu_2$ ($A_{1g} + E_{2g} = \Sigma^+_g + \Delta_g$)	RA				**1388.1**	
	ν_1 ($A_{1g} = \Sigma^+_g$)	RA			*1285.4*	**1284.6**	**1353.0**
	ν_2 ($E_{1u} = \Pi_u$)	IR	**663.7** **662.1**	**668.5** **667.9**	*667.7*	**667.8**	**673.1**
$CO^{18}O$ ($D_{\infty h}$)	ν_3 (A_{1u})	IR	**2328.6** **2322.6**	**2331.2**		**2330.4**	**2377.2**
	$2\nu_2$	RA				**1366.1**	
	ν_1 (A_{1g})	RA				**1258.5**	**1314.0**
	ν_2 (E_{1u})	IR	**658.8** **656.9**	**663.0?**		**662.8**	**667.9**
$^{13}CO_2$ ($D_{\infty h}$)	ν_3 (A_{1u})	IR	**2280.2** **2274.2**	**2282.6**		**2281.8**	**2327.3**
	$2\nu_2$	RA				**1369.7**	
	ν_1 (A_{1g})	RA				**1265.4**	**1353.0**
	ν_2 (E_{1u})	IR	**644.7** **644.3**	**649.4** **648.8**		**648.9**	**653.1**

Detailed spectra

In the following, we present the spectra of carbon dioxide (Figure S1) and methane (Figure S2) in more detail, together with the computed transitions.

The computed spectra are plotted as vertical lines. The intensities are normalized to the strongest band. For carbon dioxide this is the ν_3 fundamental. Considering the isotopoloques, the observed intensity ratios are approximately $^{13}CO_2/^{12}C^{16}O_2 = 0.03$ and $^{12}C^{18}O^{16}O/^{12}C^{16}O_2 = 0.01$. We weighted the computed spectra of the $^{13}CO_2$ and $^{12}C^{18}O^{16}O$ isotopoloques with these factors.

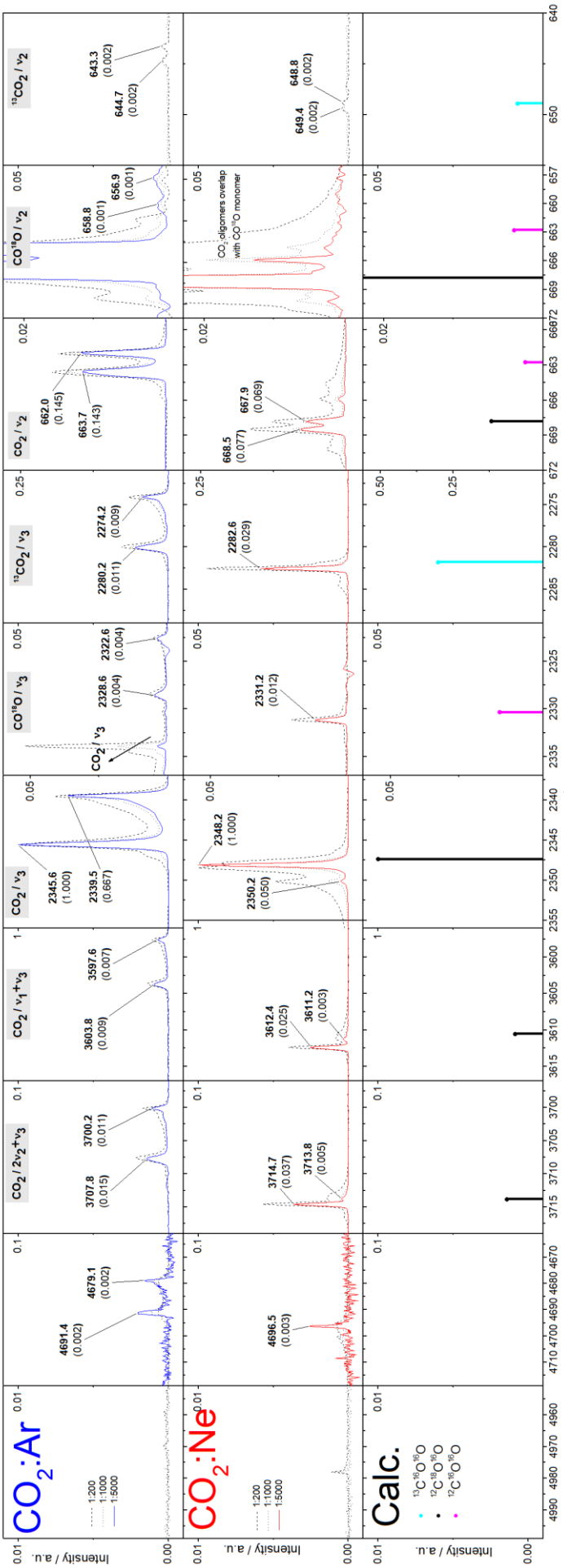

Figure S1: MI-IR spectra of $^{12}C^{16}O_2$ isolated in Ar (top, blue) and Ne (center, red) at 5.8 K. Traces of ^{13}C and ^{18}O subtitution are visible. Calculated spectra are obtained with VCI. Details on the calculations are provided in the main article.

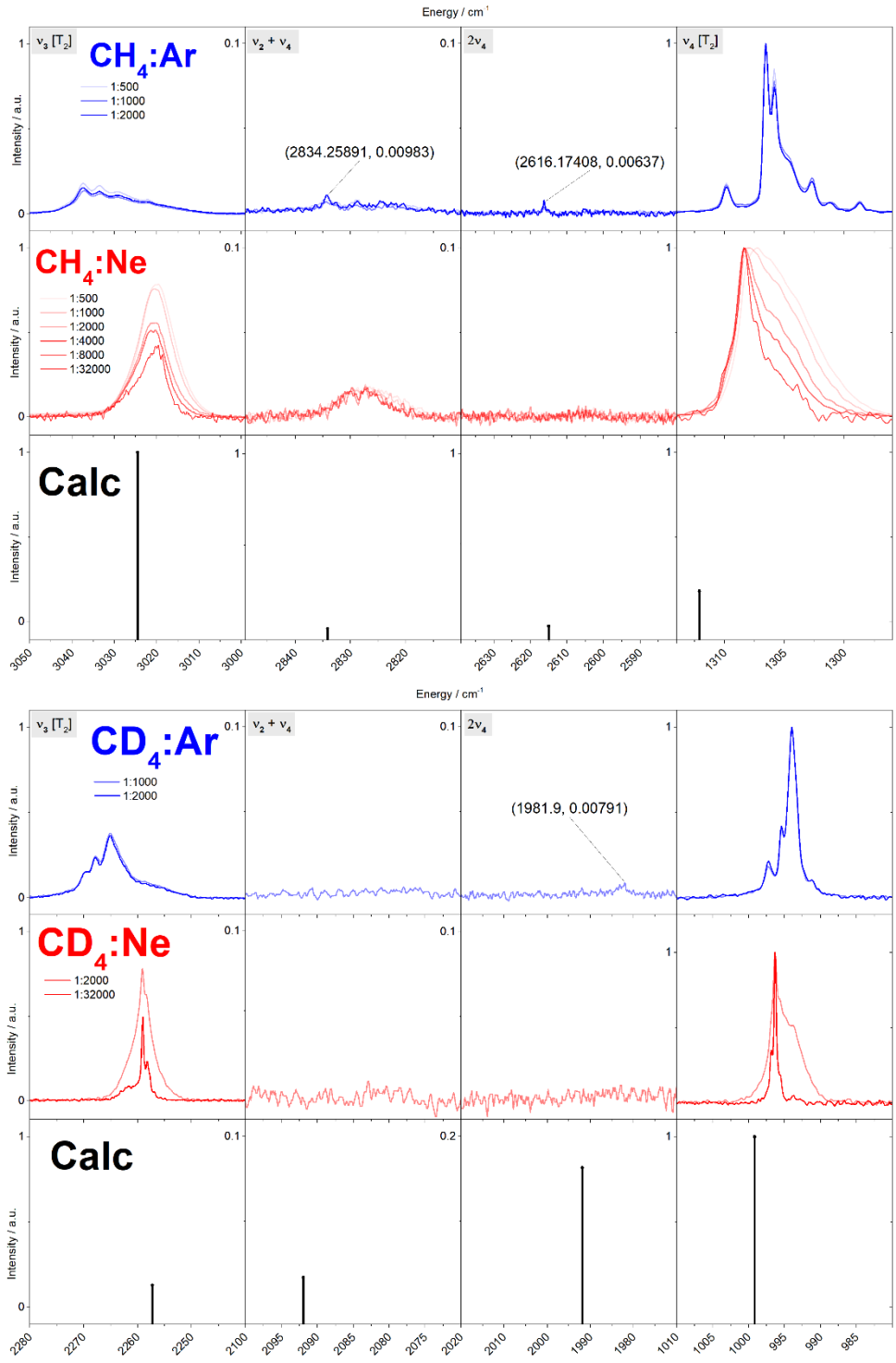

Figure S2: MI-IR spectra of $^{12}CH_4$ (top) and $^{12}CD_4$ (bottom) isolated in Ar (blue) and Ne (red) at 5.8 K. Calculated spectra are obtained with VCI. Details on the calculations are provided in the main article.