Supplementary Information

for

Influence of the Coriolis coupling on the properties of scattering resonances in symmetric and asymmetric isotopomers of ozone

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A. Technical details of calculations

The masses of oxygen isotopes used in this work are 15.99491461956 u and 17.9991596129 u for ^{16}O and ^{18}O, respectively. The conversion factor from the unified atomic mass unit (u) to kilograms is $1.660538921\times10^{-27}$ kg/u, and from atomic unit of mass to kilograms is 9.10938291×10^{-31} kg/m_e. Thus, the conversion factor from unified atomic mass unit to atomic unit of mass was obtained as a ratio of the above numbers and is equal to 1822.88848477004 m_e/u. The conversion factor from the atomic unit of energy, Hartree (E_h), to wavenumbers used in this work is 219474.6313708 cm^{-1}/E_h. The above constants are taken from [Thomas J. Bruno, Paris D. Svoronos, *CRC Handbook of Chemistry and Physics – 93rd edition* (2012)].

The potential energy surface of ozone used in this work was reported in [R. Dawes, P. Lolur, A. Li, B. Jiang, and H. Guo, J. Chem. Phys. 139, 201103 (2013)]. The computed rovibrational levels where shifted by the values of D_e = 9274.99560025014 cm^{-1} and ZPE of $^{18}O^{18}O$ = 748.9861634170745 cm^{-1} to align 0 cm^{-1} with the lower dissociation threshold of $^{18}O^{18}O^{16}O$. The values of D_e and ZPE were computed numerically.

The calculations were carried out using the following convergence parameters. The optimized DVR-grid for ρ coordinate covered the range of $3 \le \rho \le 20$ Bohr and consisted of 94 functions total. An equidistant DVR grid for θ covered the range $0.43 \le \theta \le 1.56$ rad with a total of 100 functions. The number of VBR functions for φ coordinate was 200 and the value of basis cut-off energy was set to 6000 cm^{-1}.

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The states with widths > 50 cm^{-1} as well as the states contributing less than 0.02 to Q (computed by setting $p_i = p^{SYM}_{i} + p^{ASYM}_{i} + p^{VdW(S)}_{i} + p^{VdW(A)}_{i} + p^{VdW(B)}_{i}$, the total probability) were excluded from the analysis as unphysical artefacts.

The covalent wells of the symmetric and asymmetric molecules are defined as the regions of PES with $120° \leq \varphi \leq 240°$ and $240° \leq \varphi \leq 120°$ respectively, and the values of ρ up to the position of the centrifugal barrier between the covalent and Van der Waals wells, which is generally situated around $\rho = 5.5$ Bohr. The exact position of the barrier was computed accurately based on the analysis of 2D basis functions $\mathrm{X}^{j}_{\Lambda n}$ and depends on J, Λ and a specific pathway under consideration.

The Van der Waals wells B, A and S are defined as the regions with the values of ρ from the border between the covalent and Van der Waals wells to 11 Bohr and the following values of φ:

- $-60° \leq \varphi \leq 60°$ for VdW B
- $60° \leq \varphi \leq \varphi_{bar}$ or $-\varphi_{bar} \leq \varphi \leq -60°$ for VdW A
- $\varphi_{bar} \leq \varphi \leq 360° - \varphi_{bar}$ for VdW S

The values of barrier position between VdW A and S (φ_{bar}) was found numerically by scanning the PES and are equal to $\varphi_{bar} = 117.65°$ for the singly substituted and $\varphi_{bar} = 122.35°$ for the doubly substituted ozone isotopologues. The area beyond 11 Bohr is considered a fully dissociated molecule and integrated separately from the Van der Waals area.

The value of k^{stab}_{i} is calculated as:

$$k^{stab}_{i} = \sigma^{stab} v (p^{SYM}_{i} + p^{ASYM}_{i})$$

where σ^{stab} is the stabilization cross-section taken from [M. V. Ivanov and D. Babikov, J. Chem. Phys. **144**, 154301 (2016)] as $\sigma^{stab} = 154.0326\, a_0^2$, and v is the average speed of O_3 + Ar system:

$$v = \sqrt{\frac{8kT}{\pi \mu_{stab}}}$$

where μ_{stab} is the reduced mass of O_3 + Ar system:

$$\mu_{stab} = \frac{m(O_3) m(Ar)}{m(O_3) + m(Ar)}$$

where $m(O_3)$ and $m(Ar)$ are the masses of O_3 and Ar, respectively.

All values of Q in this work are computed for $T = 298$ K and $[M] = 6.53 * 10^{24}$ m^{-3}.

The operators in Eq. (1) of the main text are defined as follows:

$$\hat{T}_{\rho} = -\frac{\hbar^2\,\partial^2}{2\mu\partial\rho^2}$$

$$\hat{T}_{\theta} = -\frac{2\hbar^2\,\partial^2}{\mu\rho^2\partial\theta^2}$$

$$\hat{T}_{\varphi} = -\frac{2\hbar^2 \qquad \partial^2}{\mu\rho^2\sin^2\theta\partial\phi^2}$$

$$V_{ext} = -\frac{\hbar^2}{2\mu\rho^2}\left(\frac{1}{4} + \frac{4}{\sin^2 2\theta}\right)$$

$$\hat{T}_{sym} = \frac{A+B}{2}\hat{J}^2 + \left(C - \frac{A+B}{2}\right)\hat{J}_z^2$$

$$\hat{T}_{asym} = \frac{A-B}{2}\left(\hat{J}_x^2 - \hat{J}_y^2\right)$$

$$\hat{T}_{cor} = 4B\cos\theta\left(i\hbar\frac{\partial}{\partial\varphi}\right)\hat{J}_y$$

B. The treatment of doubly substituted case

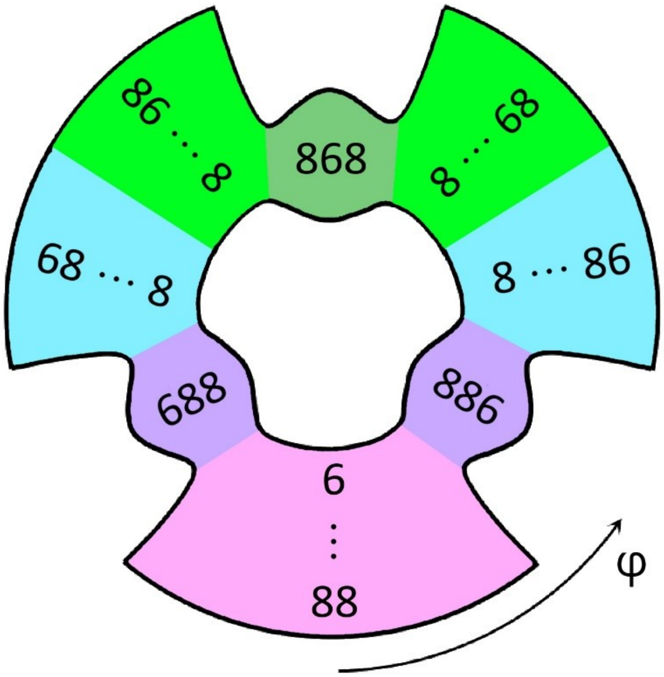

Figure S1: Same as **Figure 1** in the main text, but for the doubly substituted case.

Table S1: Same as **Table 1** in the main text, but for the doubly substituted case.

Color in Figure S1	Meaning	Probability
Green	Covalently bound symmetric ozone molecule $^{18}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	p_i^{SYM}
Purple	Covalently bound asymmetric ozone molecules $^{18}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	p_i^{ASYM}
Light blue	Van der Waals complex in the $^{18}\mathrm{O} + {}^{18}\mathrm{O}^{16}\mathrm{O}$ channel, near asymmetric $^{18}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	$p_i^{VdW(A)}$
Light green	Van der Waals complex in the $^{18}\mathrm{O}^{16}\mathrm{O} + {}^{18}\mathrm{O}$ channel, near symmetric $^{18}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	$p_i^{VdW(S)}$
Pink	Van der Waals complexes in the $^{18}\mathrm{O}^{18}\mathrm{O} + {}^{16}\mathrm{O}$ channel	$p_i^{VdW(B)}$

C. Properties of scattering resonances localized over the covalent well of ozone

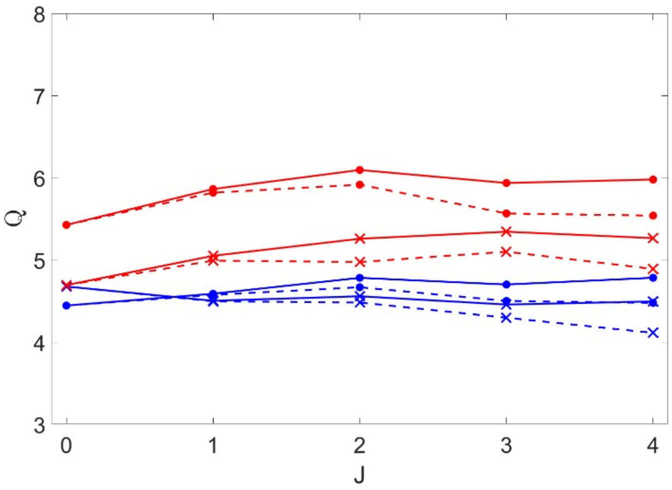

Figure S2: Partition function Q of scattering resonances in ozone as a function of rotational excitation up to $J = 4$. Only the states localized over the covalent well are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The dots (x-symbols) correspond to symmetric (asymmetric) isotopomers. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

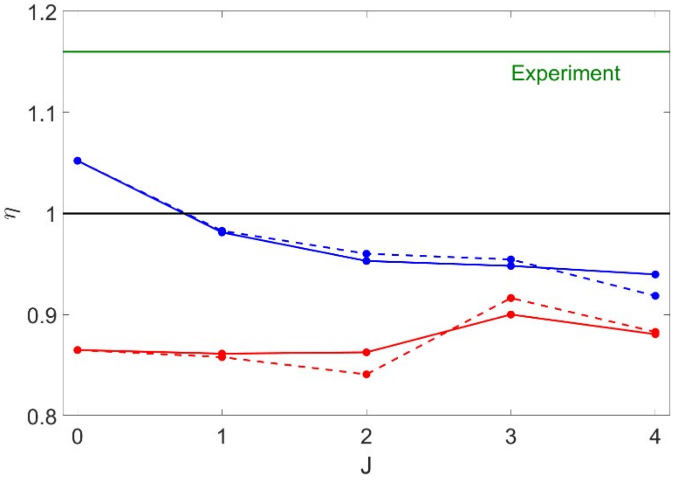

Figure S3: Symmetry driven isotope effect η in ozone as a function of rotational excitation up to $J = 4$. Only the states localized over the covalent well are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

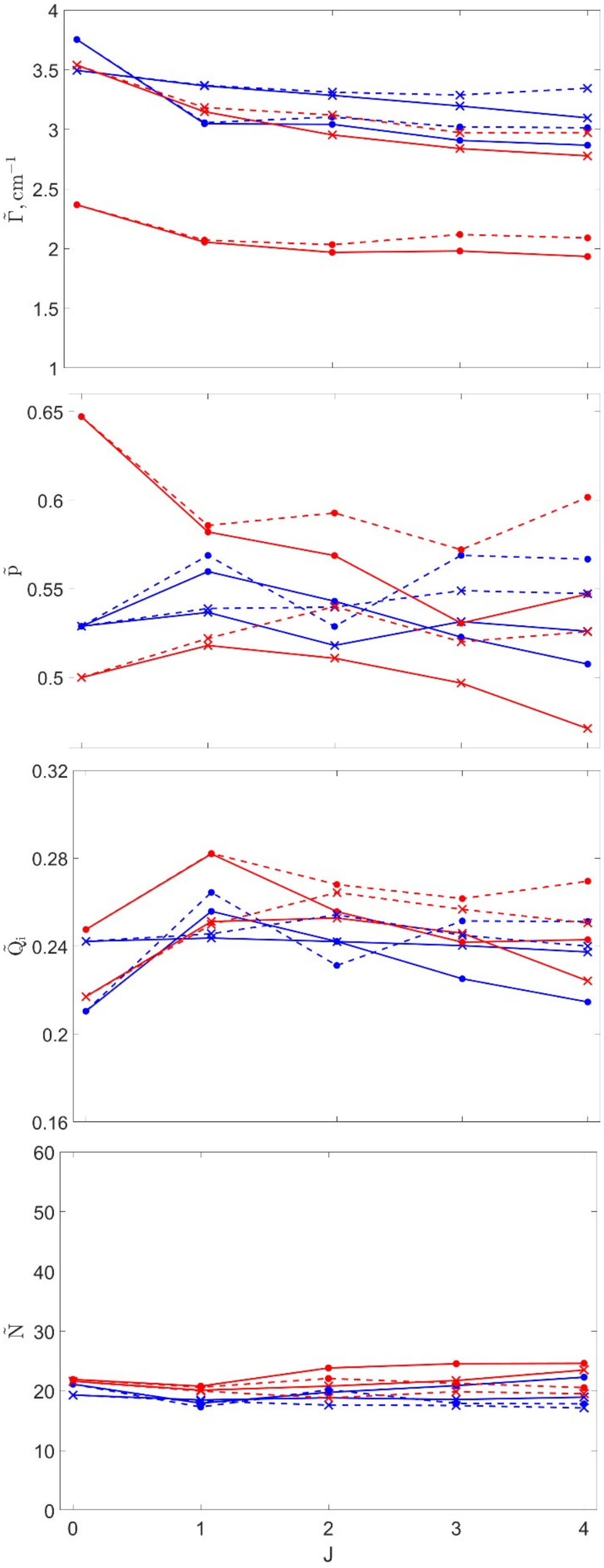

Figure S4: The average properties $\tilde{\Gamma}$, $\tilde{p}$, $\tilde{Q}_i$ and $\tilde{N}$ of scattering resonances in ozone (see text) as a function of rotational excitation up to $J = 4$. Only the states localized over the covalent well are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The dots (x-symbols) correspond to symmetric (asymmetric) isotopomers. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

D. Properties of scattering resonances distributed over the Van der Waals region of the PES

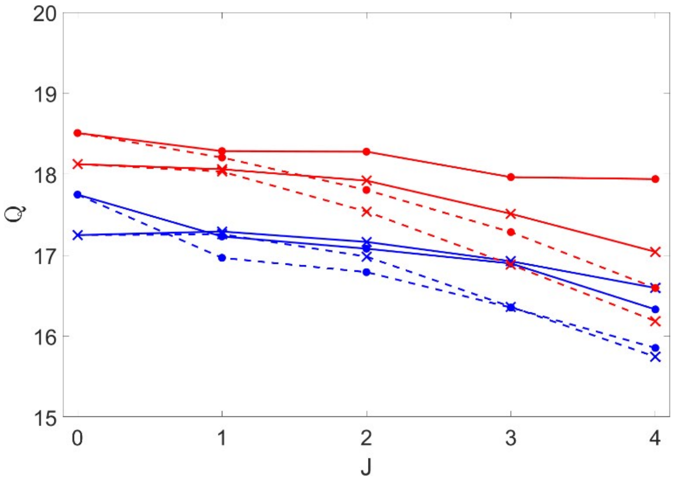

Figure S5: Partition function Q of scattering resonances in ozone as a function of rotational excitation up to $J = 4$. Only the states localized over the Van der Waals region of the PES are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The dots (x-symbols) correspond to symmetric (asymmetric) isotopomers. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

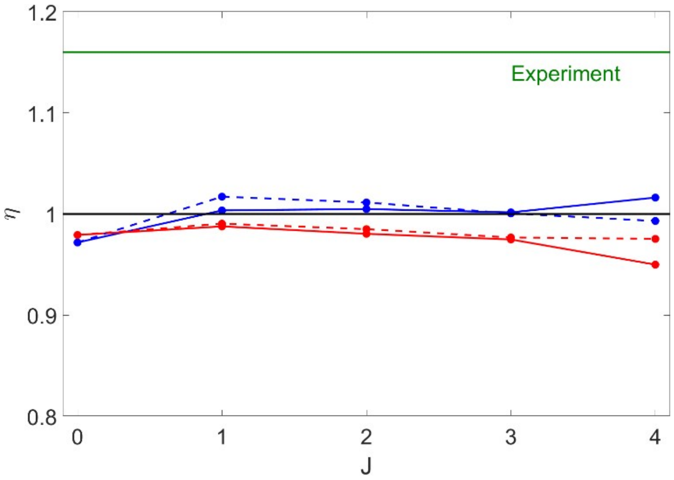

Figure S6: Symmetry driven isotope effect η in ozone as a function of rotational excitation up to $J = 4$. Only the states localized over the Van der Waals region of the PES are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

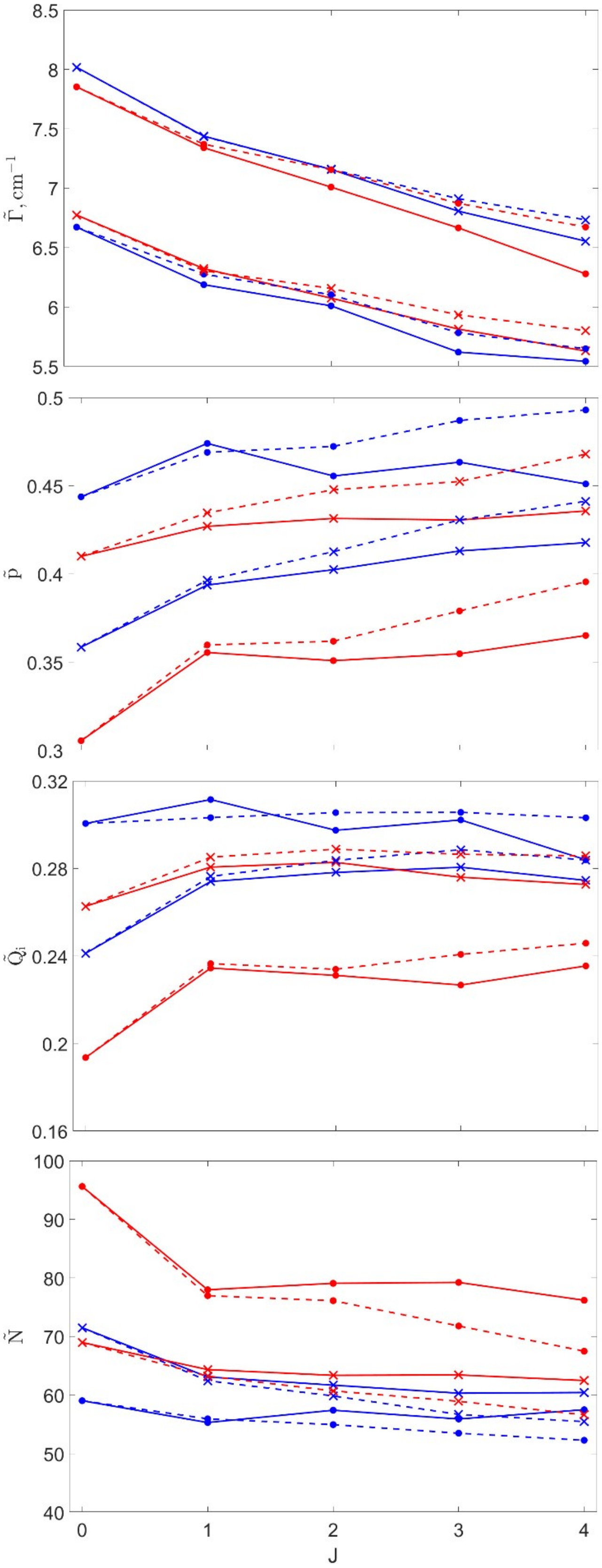

Figure S7: The average properties $\tilde{\Gamma}$, $\tilde{p}$, $\tilde{Q}_i$ and $\tilde{N}$ of scattering resonances in ozone (see text) as a function of rotational excitation up to $J = 4$. Only the states distributed over the Van der Waals region of the PES are included. The blue (red) color corresponds to the singly (doubly) substituted isotopologues of ozone. The dots (x-symbols) correspond to symmetric (asymmetric) isotopomers. The solid (dashed) lines correspond to the accurate coupled rotation-vibration (approximate symmetric-top rotor) calculations.

E. Description of the data archive (raw outputs of the SpectrumSDT)

The files are organized into folders. The two root folders correspond to the kind of calculation (rovibrationally coupled or uncoupled). The next level corresponds to calculations of either singly substituted ozone (both $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$, labelled as "686") or doubly substituted ozone (both $^{18}O^{16}O^{18}O$ and $^{16}O^{18}O^{18}O$, labelled as "868"). Lower level folders specify the following values:

- J (rotational quantum number),
- Λ (projection of J). Specified for the symmetric top rotor only, since Λ is not a good quantum number in the coupled calculations. "K" is used in folder names and file headers instead of "Λ",
- parity (0 or 1). Specified for coupled calculations only, since the two parities are degenerate in the symmetric top rotor approximation,
- vibrational symmetry of the wave functions. Either symmetric (labelled "even"), or antisymmetric (labelled "odd").

If a particular combination of these parameters if not allowed, then the corresponding folder is absent.

Each folder contains one file with the output of SpectrumSDT for given parameters. Each row in the file represents a state. The first column contains its energy (in cm^{-1}). The second and third columns contain the two components of its width: in the channel A+S (asymmetric O_2) and B (symmetric O_2), respectively (in cm^{-1}). The total width (Γ_i) can be obtained as their sum. The columns 4 to 9 contain wave function probabilities in the following regions in this order: symmetric covalent well, asymmetric covalent wells, VdW(S), VdW(A), VdW(B), and in the asymptotic (free molecule) region. The remaining $J + 1$ columns contain wave function probabilities associated with each value of Λ.