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

Electronic Supplementary Information

Cryogenic fluorescence spectroscopy of oxazine ions isolated *in vacuo*

Christina Kjær,*[a] Emil Vogt,[b] Jeppe Langeland,[a] Nanna Falk Christensen,[b] Thomas Toft Lindkvist,[a] Henrik G. Kjaergaard,[b] and Steen Brøndsted Nielsen[a]

[a.] Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark. Email: christina.kjaer@phys.au.dk
[b.] Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark.

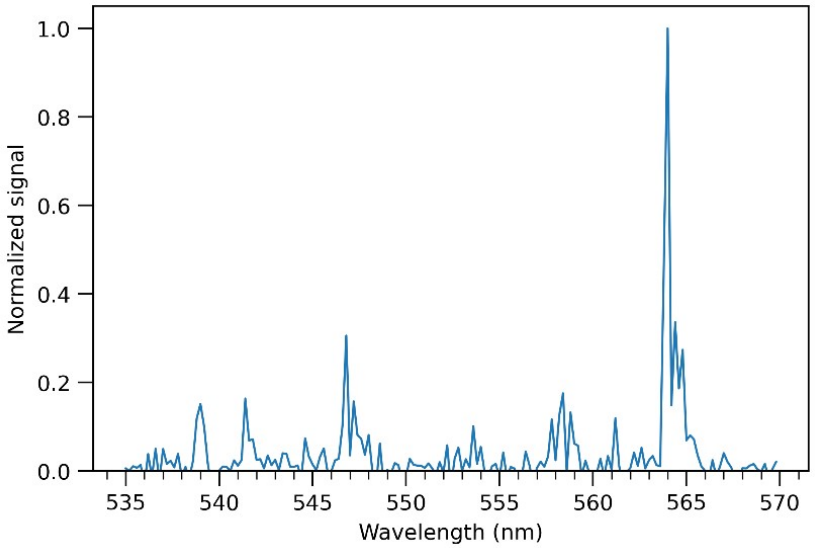

Fig. S1. Fluorescence-excitation spectrum of cold (100 K) **R**$^-$ obtained at low laser power (<0.01 mW).

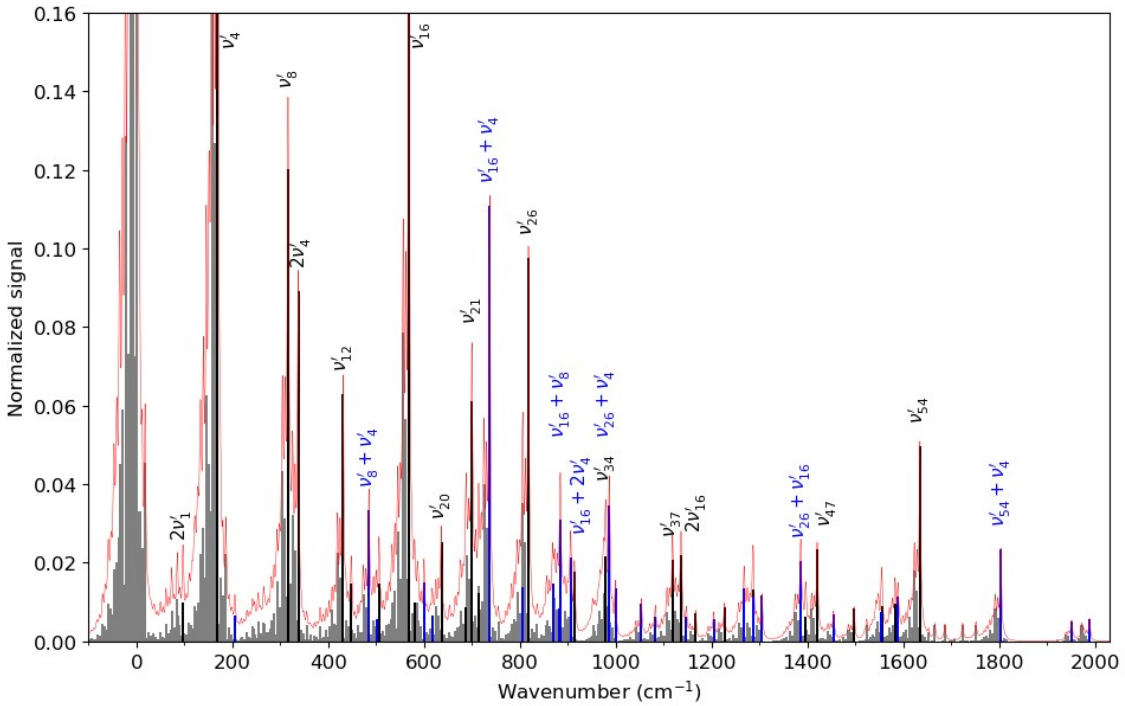

Fig. S2. Simulated Franck-Condon absorption spectrum of **R**$^{-}$ at 100 K obtained using B3LYP/aug-cc-pVTZ time-dependent density function theory. All transitions (grey) contributing to the total simulated absorption spectrum (red). The black transitions are significant transitions from the vibrational ground state (0'') to the final state indicated by the labels (v'). Blue transitions involve combinations of two or more of the black transitions.

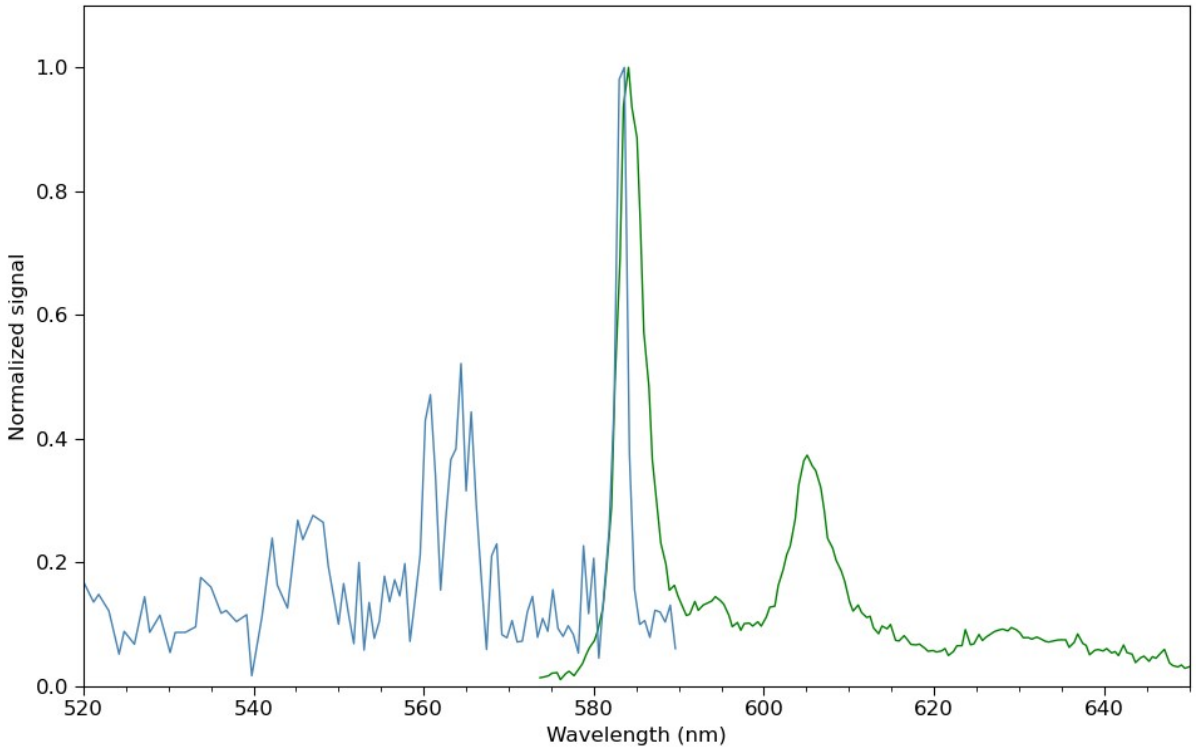

Fig. S3. 100 K fluorescence-excitation spectrum (blue) of gaseous **Ox-170**$^{+}$ obtained with lower laser power (<0.03mW) than the spectrum shown in Fig. 5.

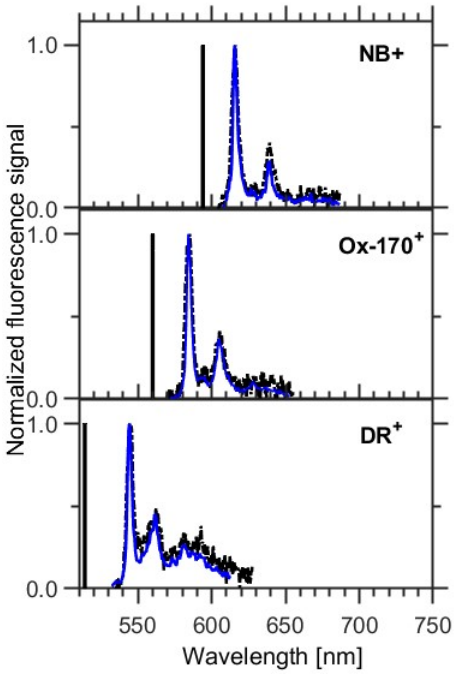

Fig. S4. Low-temperature fluorescence spectra obtained at LUNA2 using two different spectrometers combined with an iCCD camera. Black spectra were obtained with a shamrock spectrometer and blue spectra with a kymera spectrometer.

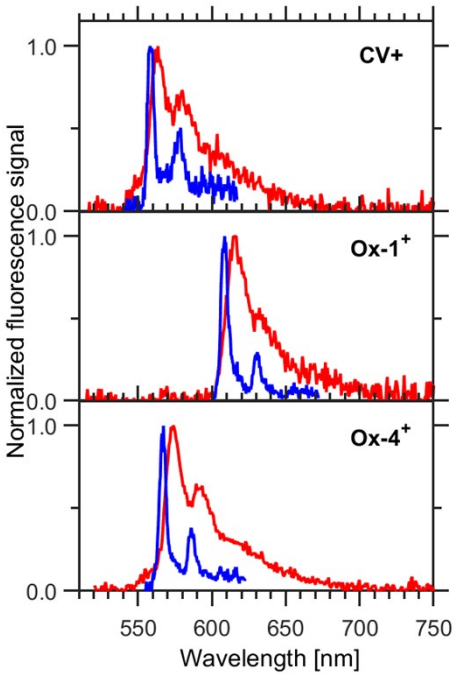

Fig. S5. Fluorescence spectra obtained at room temperature (red) and at 100 K (blue). Room-temperature spectra were obtained with the LUNA instrument[1] and taken from.[2] Low-temperature spectra were obtained with the LUNA2-instrument using a shamrock spectrometer combined with an iCCD camera, whereas the LUNA instrument is equipped with a shamrock spectrometer and a CCD camera.

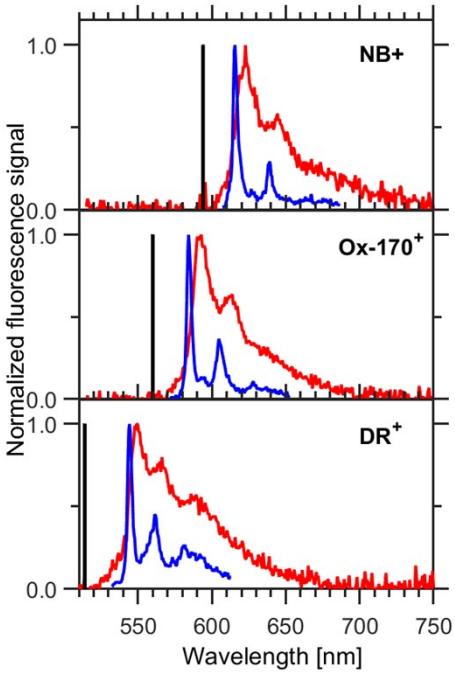

Fig. S6. Fluorescence spectra obtained at room temperature (red) and at 100 K (blue). The black lines indicate excitation wavelengths which were 594 nm (**NB**$^+$), 561 nm (**Ox-170**$^+$), and 514 nm (**DR**$^+$). Room-temperature spectra were obtained using the LUNA instrument. Low-temperature spectra were obtained using the LUNA2 instrument with a Kymera spectrometer combined with an iCCD camera.

Mode	S_0 [cm^{-1}]	S_1 [cm^{-1}]	Mode	S_0 [cm^{-1}]	S_1 [cm^{-1}]	Mode	S_0 [cm^{-1}]	S_1 [cm^{-1}]
1	59.7	48.2	21	726.5	699.6	41	1296.1	1226.8
2	84.3	77.7	22	749.8	700.3	42	1302.4	1241.7
3	178.0	157.1	23	757.5	714.0	43	1328.8	1285.7
4	185.4	168.7	24	780.0	745.4	44	1368.4	1292.9
5	186.5	172.2	25	834.2	787.9	45	1419.5	1357.1
6	255.3	253.7	26	835.1	817.8	46	1454.2	1396.6
7	304.3	303.2	27	854.3	819.0	47	1484.4	1420.2
8	349.5	316.3	28	875.9	853.3	48	1504.3	1435.6
9	356.0	341.1	29	876.4	858.9	49	1538.3	1497.1
10	443.6	343.4	30	877.2	863.1	50	1558.0	1523.3
11	453.9	428.7	31	905.7	897.7	51	1599.2	1539.0
12	460.7	431.1	32	950.9	913.8	52	1608.4	1555.1
13	469.5	436.8	33	986.7	958.7	53	1632.7	1582.8
14	473.6	448.0	34	987.0	978.5	54	1678.9	1634.6
15	526.7	506.1	35	1106.7	979.2	55	3155.2	3150.6
16	578.7	568.2	36	1122.0	1106.1	56	3155.5	3154.4
17	590.0	580.4	37	1160.0	1118.4	57	3176.1	3174.1
18	639.9	616.0	38	1160.9	1159.0	58	3176.5	3179.2
19	661.8	633.1	39	1227.6	1166.6	59	3185.0	3181.9
20	678.1	636.2	40	1251.0	1213.2	60	3185.5	3191.8

Table. S1. B3LYP/aug-cc-pVTZ calculated harmonic transition wavenumbers in S_0 and S_1 of $\mathbf{R}^-$. The modes in increasing energy order for both S_0 and S_1. The Duschinsky matrix that is needed to correlate the modes is provided in the repository.

Ion	$\mathbf{NB}^+$	$\mathbf{Ox\text{-}1}^+$	$\mathbf{Ox\text{-}170}^+$	$\mathbf{Ox\text{-}4}^+$	$\mathbf{CV}^+$	$\mathbf{DR}^+$	$\mathbf{R}^-$
Calculated $S_0 \rightarrow S_1$ excitation wavelengths (nm)	510.4	506.5	494.8	467.4	479.4	483.6	457.6

Table. S2. Calculated vertical $S_0 \rightarrow S_1$ excitation energies at the B3LYP/aug-cc-pVTZ level of theory for all ions under study.

References

1 M. H. Stockett, J. Houmøller, K. Støchkel, A. Svendsen and S. Brøndsted Nielsen, *Rev. Sci. Instrum.*, 2016, **87**, 53103.

2 C. Kjær and S. Brøndsted Nielsen, *Phys. Chem. Chem. Phys.*, 2019, **21**, 4600–4605.