

# In Search of Molecular Ions for Optical Cycling: A Difficult Road.

## Supplemental Material.

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### Computational details

All electronic structure calculations were performed using the *Q-Chem* package<sup>1,2</sup>, except for EOM-IP-CCSDT, which were carried out with *Cfour*<sup>3</sup>.

Radiative lifetimes are determined by the transition dipole moment ( $\mu_{IF}$ ) and frequency of the transition ( $\omega_0$ ), as given by Einstein's coefficients  $A_{ba}$ :

$$A_{ba} = \frac{g_a \omega_0^3 \mu_{IF}^2}{3\hbar\pi c^3 \varepsilon_0}, \quad (1)$$

where  $g_a$  is the degeneracy of the lower state.

TABLE S1: Einstein's coefficients for  $A^2\Pi - X^2\Sigma^+$  transition in CaF and SrF computed by Eq. (1) using  $\omega_0$  and  $\mu_{IF}$  obtained from EOM-EA-CCSD calculations. The computed values are compared with the experimentally<sup>4</sup> determined values for the  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$  states.

Molecule	$E_{ex}$ , eV	$\mu_{IF}$ , au	$A_{ba}$ , MHz	State	$\tau$ , ns	$\Gamma$ , MHz
CaF	2.100	2.268	50.7	$A^2\Pi_{1/2}$	21.9	45.7
				$A^2\Pi_{3/2}$	18.4	54.3
SrF	1.905	2.437	43.6	$A^2\Pi_{3/2}$	24.1	41.5
				$A^2\Pi_{3/2}$	22.6	44.2

One can also compute spontaneous decay rates relative to a reference system. Specifically, we can use the computed values of  $\omega_0$  and  $\mu_{IF}$  and scale the experimentally determined spontaneous decay rate of the  $A^2\Pi_{1/2}$  state in SrF:

$$\gamma_{eff} = g_a \left[ \frac{\omega_0}{\omega_0(\text{SrF})} \right]^3 \left[ \frac{\mu_{IF}}{\mu_{IF}(\text{SrF})} \right]^2 \Gamma(\text{SrF}), \quad (2)$$

where  $\gamma_{eff}$  is an effective spontaneous decay rate,  $\omega_0$  and  $\mu_{IF}$  are resonant frequency and transition dipole moment of a molecule computed using EOM-CC;  $\omega_0(\text{SrF})$  and  $\mu_{IF}(\text{SrF})$  are resonant frequency and transition dipole moment computed for  $X^2\Sigma^+-A^2\Pi$  transition in SrF;  $\Gamma(\text{SrF}) = 2\pi \times 7$  MHz is an experimental value of the spontaneous decay rate of the  $A^2\Pi_{1/2}$  state in SrF.

TABLE S2: Comparison of Einstein’s coefficients  $A_{ba}$  with the effective spontaneous decay rates  $\gamma_{eff}$  computed using EOM-EA-CCSD for several selected molecules with similar electronic structure of the states involved in the excitation.

Molecule	$A_{ba}$ , MHz	$\gamma_{eff}$ , MHz
YF <sup>+</sup>	228.0	229.7
YOH <sup>+</sup>	209.3	211.0
AlCl <sup>+</sup>	91.3	92.1
GaCl <sup>+</sup>	67.9	68.4
InCl <sup>+</sup>	70.8	71.4

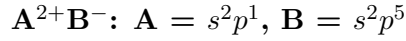


TABLE S3: Total electronic energies (at respectively optimized geometry),  $T_2^2$  diagnostic, equilibrium bond length  $r_e$  of AlCl<sup>+</sup>, GaCl<sup>+</sup>, and InCl<sup>+</sup> in the ground electronic state calculated using EOM-EA-CCSD and EOM-IP-CCSD.

EOM-CC	AlCl <sup>+</sup>			GaCl <sup>+</sup>			InCl <sup>+</sup>		
	$E$ , Hartree	$T_2^2$	$r_e$	$E$ , Hartree	$T_2^2$	$r_e$	$E$ , Hartree	$T_2^2$	$r_e$
EOM-EA-CCSD	-701.695907	0.1258	2.015	-718.547498	0.1715	2.076	-649.389095	0.1967	2.279
EOM-IP-CCSD	-701.692874	0.1604	2.023	-718.545800	0.1851	2.086	-649.383885	0.2073	2.296

$$\mathbf{AB}^+: \mathbf{A} = s^2p^1, \mathbf{B} = s^1$$

TABLE S4: Dissociation reactions and corresponding dissociation energies of  $\mathbf{AB}^+$  ( $\mathbf{A} = \mathbf{B}, \mathbf{Al}, \mathbf{Ga}; \mathbf{B} = \mathbf{H}, \mathbf{Li}$ ). Energies of  $\mathbf{B}^+, \mathbf{Al}^+, \mathbf{Ga}^+, \text{ and } \mathbf{Li}^+$  are calculated using CCSD. Energies of  $\mathbf{B}, \mathbf{Al}, \mathbf{Ga}, \text{ and } \mathbf{Li}$  are calculated using EOM-EA-CCSD.

Reaction	$E_{dis}$ , eV
$\mathbf{BH}^+ \rightarrow \mathbf{B}^+ + \mathbf{H}$	2.09
$\mathbf{AlH}^+ \rightarrow \mathbf{Al}^+ + \mathbf{H}$	0.74
$\mathbf{GaH}^+ \rightarrow \mathbf{Ga}^+ + \mathbf{H}$	0.26
$\mathbf{BLi}^+ \rightarrow \mathbf{B}^+ + \mathbf{Li}$	3.67
$\mathbf{AlLi}^+ \rightarrow \mathbf{Al}^+ + \mathbf{Li}$	1.69
$\mathbf{GaLi}^+ \rightarrow \mathbf{Ga}^+ + \mathbf{Li}$	1.66
$\mathbf{BLi}^+ \rightarrow \mathbf{B} + \mathbf{Li}^+$	0.81
$\mathbf{AlLi}^+ \rightarrow \mathbf{Al} + \mathbf{Li}^+$	1.18
$\mathbf{GaLi}^+ \rightarrow \mathbf{Ga} + \mathbf{Li}^+$	1.17

$$[\mathbf{AB}]^+: \mathbf{A} = s^2p^2, \mathbf{B} = s^2p^4$$

TABLE S5: Vertical IEs (eV) of SiO, SiS, and SiSe computed using EOM-IP-CC methods with the aug-cc-pVTZ basis set in comparison with the literature values.

SiO	EOM-IP-CCSD	EOM-IP-CCSD(T)(a)*	EOM-IP-CCSDT	Ref. 5
$1^2\Sigma^+$	11.5178	11.4044	11.4130	11.61
$1^2\Pi$	12.0535	12.0522	12.0041	12.19
$2^2\Sigma^+$	15.1104	14.7287	14.6544	14.80
SiS	EOM-IP-CCSD	EOM-IP-CCSD(T)(a)*	EOM-IP-CCSDT	Ref. 6
$1^2\Sigma^+$	10.5011	10.4125	10.4073	10.56
$1^2\Pi$	10.5823	10.5692	10.5600	10.53
$2^2\Sigma^+$	14.4522	14.0846	13.8370	13.88
SiSe	EOM-IP-CCSD	EOM-IP-CCSD(T)(a)*	EOM-IP-CCSDT	Ref. 7
$1^2\Sigma^+$	10.1510	10.0557	10.0552	10.00
$1^2\Pi$	10.1172	10.1155	10.1090	9.98
$2^2\Sigma^+$	14.1808	13.7459	13.4071	13.20

TABLE S6: Equilibrium bond lengths ( $\text{\AA}$ ) of the  $X^2\Sigma^+$ ,  $A^2\Pi$ , and  $B^2\Sigma^+$  states in SiO<sup>+</sup> calculated using EOM-IP-CCSD/aug-cc-pVTZ in comparison with the literature values.

	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$
EOM-IP-CCSD	1.526	1.640	1.506
Exp. <sup>8,9</sup>	1.519	1.637	1.527

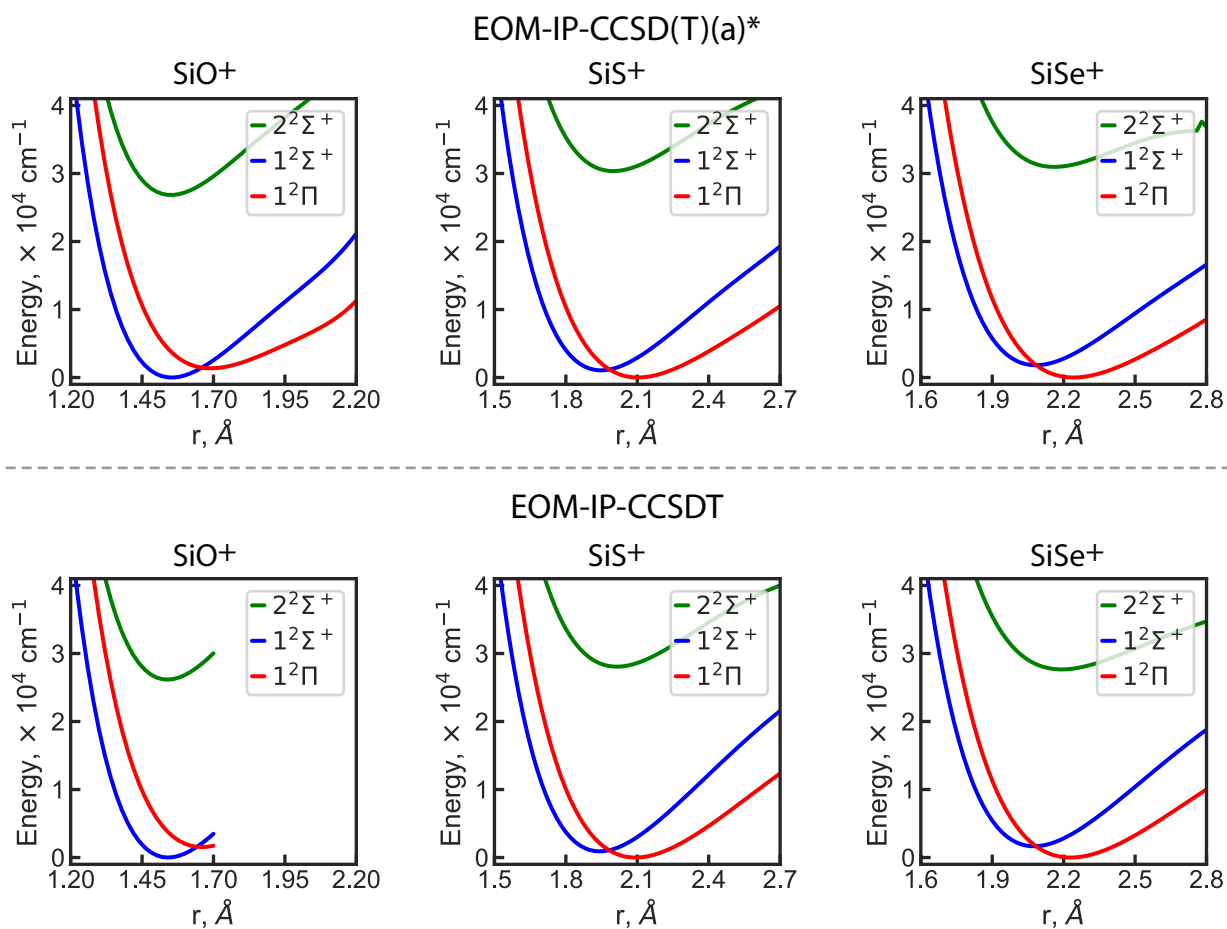


FIG. S1: Potential energy curves of SiO<sup>+</sup>, SiS<sup>+</sup>, and SiSe<sup>+</sup> calculated using EOM-IP-CCSD(T)(a)\* and EOM-IP-CCSDT using the aug-cc-pVTZ basis set.

$$[\mathbf{AB}]^+: \mathbf{A} = s^2p^3, \mathbf{B} = s^2p^3$$

TABLE S7: Comparison of the equilibrium bond lengths ( $r_e$ , Å),  $T_e$  constant (eV) and FCFs of  $\text{N}_2^+$  calculated using EOM-IP-CCSD with experimental data.

	EOM-IP-CCSD	Exp.
$r_e(X^2\Sigma_g^+)$	1.110	1.116
$r_e(A^2\Pi_u)$	1.161	1.175
$r_e(B^2\Sigma_u^+)$	1.067	1.074
$T_e(A^2\Pi_u)$	1.364	1.137
$T_e(B^2\Sigma_u^+)$	3.205	3.157
$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$		
0 $\rightarrow$ 0	0.6197	0.6481
0 $\rightarrow$ 1	0.3128	0.2619
0 $\rightarrow$ 2	0.0616	0.0705
$A^2\Pi_u \rightarrow X^2\Sigma_g^+$		
0 $\rightarrow$ 0	0.5567	0.4974
0 $\rightarrow$ 1	0.3060	0.3718
0 $\rightarrow$ 2	0.1030	0.1116

TABLE S8: Comparison of the vertical IEs of  $\text{PN}$ ,  $T_e$  constants and equilibrium bond lengths of  $\text{PN}^+$  calculated using EOM-IP-CCSD with experimental data.

	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$
IE, eV			
EOM-IP-CCSD	11.868	12.478	16.434
Exp. <sup>10</sup>	11.88	12.30	15.74
$T_e$ , eV			
EOM-IP-CCSD	0.000	0.513	4.538
Exp. <sup>10</sup>	0.000	0.42	3.86
$r_e$ , Å			
EOM-IP-CCSD	1.484	1.552	1.465
Exp. <sup>10</sup>	1.50	1.565	1.45

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