Appendices

APPENDIX A MOLECULAR SPECTROSCOPY

We list in Table A1 the details of the spectroscopy used to fit the molecular emission of the different species analysed in this work. We have used entries from the Cologne Database for Molecular Spectroscopy (CDMS,Endres et al. 2016) and the Jet Propulsion Laboratory (JPL; Pickett et al. 1998), which are based on the laboratory works and theoretical calculations indicated in Table A1.

Table A1. Spectroscopy of the molecules analysed in this work. The molecular catalog, number and date of the entry, and the references for the line lists and dipole moments are listed.

Molecule	Catalog	Entry	Date	Line list ref.	Dipole moment ref.
PO^+	JPL	47005	December 1996	Petrmichl et al. (1991)	Peterson and Woods (1990); this work
PO	CDMS	47507	October 2019	Kawaguchi et al. (1983), Bailleux et al. (2002)	Kanata et al. (1988)
SO^+	JPL	48010	December 1996	Amano et al. (1991)	Turner (1992), from Peterson & Woods, priv. comm; this work
^{34}SO	CDMS	50501	August 1998	Tiemann (1974)	Powell and Lide (1964), Lovas et al. (1992)^a
$S^{18}O$	CDMS	50502	August 1998	Tiemann (1974)	Powell and Lide (1964), Lovas et al. (1992)^a
NO^+	CDMS	30512	January 2017	Bowman et al. (1982)	Polák and Fišer (2004)
NO	CDMS	30517	January 2015	Müller et al. (2015)	Neumann (1970)

(a) The dipole moment of SO was used.

APPENDIX B CALCULATION OF THE PO$^+$ DIPOLE MOMENT

Due to the lack of experimental measurements of permanent dipole for the ion PO$^+$, quantum chemical calculations are needed to obtain it. There are previous theoretical calculations of the permanent dipole moment for the cation PO$^+$($^1\Sigma$) (Peterson and Woods 1990), who derived a value of μ=3.44. This is the value used in the JPL molecular database entry (47005, December 1996) of PO$^+$ (see Table A1). In this work we have carried out new calculations for updating this value. Thus, we optimized the PO$^+$ ($^1\Sigma$) with the CCSD(T)-F12 method (Adler et al., 2007; Knizia et al., 2009). With the inclusion of the explicit F12 electronic correlation, we can obtain results near the basis set limit with smaller basis sets. To do this, we selected de cc-pVTZ-F12 and cc-pVTZ-F12-CABS as orbital basis set and complete auxiliary basis set respectively. For the correlation and coulomb fitting we increase the size of the basis set to the augmented aug-cc-pVQZ. The coupled cluster calculations showed that the T_1 diagnostic obtained for this molecule is 0.025. The T1 diagnostic is an indicator of the multi-configurational character of a chemical species (Lee and Taylor, 1989). When this value exceeds 0.020 for a closed shell system or 0.045 for an open shell system, multi-configurational methods are needed to correctly describe the wavenfunction (Rienstra-Kiracofe et al., 2000). In this case, 0.025 lies above the limit for a closed shell system. Thus, our new, and previous coupled cluster calculations (Moussaoui et al., 2003), and those computed with quadratic CI methods (Peterson and Woods, 1990) were not taking into account herein, since multi-configurational calculations are needed to correctly describe this molecule. Recently, high level multi-configurational calculations have been carried out to describe electronic spectroscopic properties of the PO$^+$ cation like transition dipole moments between different electronic states (Zhang and Shi, 2021). Previously, multiconfigurational CASSCF calculations have been carried out to compute the permanent dipole moment of PO$^+$ (Moussaoui et al., 2003). However dynamic correlation in the inactive orbitals were not taken into account.

In this sense, we optimized the geometry of PO$^+$($^1\Sigma$) with the fully internally contracted CASPT2 method (Andersson et al., 1990; Roca-Sanjuán et al., 2012). For the selection of the active orbitals we chose a full valence active space, namely, the four $4s$ and $4p$ electrons of phosphorous cation and the six $3s$ and $3p$ electrons of oxygen, leaving a (10e,8o) active space. This system has a non-negligible basis set dependence, then, we started the calculation of CASPT2(10e,8o) in combination with the correlation-consistent basis set aug-cc-pVTZ (Kendall et al., 1992), up to the 6Z (Woon and Dunning, 1993; Peterson et al., 1994; Wilson et al., 1996).

Table B1 shows the computed equilibrium distance ($r_{\mathrm{P-O}}$), harmonic frequency (ν), rotational constant (B_e) and the dipole moment (μ) for the cation PO$^+$($^1\Sigma$). The value of the permanent dipole (μ) used in this work is 3.131 D, computed at the full valence CASPT2(10e,8o)/aug-cc-pV6Z. From previous calculations, the most similar result was obtained with the CASSCF(10e,8o) (Moussaoui et al., 2003).

Table B1. Equilibrium distance ($r_{\mathrm{P-O}}$), harmonic frequency (ν), rotational constant (B_e), and the dipole moment (μ) for the cation PO$^+$($^1\Sigma$).

Basis set	$r_{\mathrm{P-O}}$ (Å)	ν (cm^{-1})	B_e (MHz)	μ (Debye)
CCSD(T)-F12/cc-pVTZ-F12^a	1.4283	1415.18	23481.93937	3.043
CASPT2(10e,8o)/aug-cc-pVTZ	1.4418	1379.44	23043.79083	3.107
CASPT2(10e,8o)/aug-cc-pVQZ	1.4339	1389.61	23300.21209	3.120
CASPT2(10e,8o)/aug-cc-pV5Z	1.4274	1402.29	23510.57499	3.129
CASPT2(10e,8o)/aug-cc-pV6Z	1.4256	1412.27	23570.90768	3.131
Exp. (Dyke et al., 1982)	1.4249	1411.50	—-	—-

(a) For the correlation and coulomb fitting the augmented aug-cc-pVQZ was used.

APPENDIX C CALCULATION OF THE SO$^+$ DIPOLE MOMENT

The SO$^+$ entry (48010, December 1996) of the JPL molecular database assumed a value of 1.0 for the dipole moment. Therefore, the derived column density has to be corrected using the true value of the dipole moment. As in the case of PO$^+$ (Zhang and Shi, 2021), transition dipole moments between different electronic states has been computed, obtaining theoretical results in agreement with experiments (Ben Houria et al., 2006; Xing et al., 2012). However, permanent dipole moment measurement for the SO$^+$($^2\Pi$) is needed. Turner (1992) used a value of the dipole moment μ=2.30 D obtained by Peterson & Woods (priv. comm.). However, no data about the followed methodology have been found. To obtain a reliable value of the dipole moment, we optimized the SO$^+$ cation in its doublet ground state ($^2\Pi$) with the above mentioned coupled cluster method but using the resolution-of-identity (RI) approach for the correlation integrals (Feyereisen et al., 1993) and with the cc-pVQZ-F12 and cc-pVQZ-F12-CABS basis sets. Although the cation SO$^+$($^2\Pi$) is an open shell system, the T_1 diagnostic found for this molecule is 0.022, far from the limit for an open shell system (0.045). Table C1 shows the comparison of our coupled cluster calculations with the available experimental results. The derived dipole moment for the SO$^+$($^2\Pi$) cation obtained and used in this work is 2.016 D, 0.284 D lower than the previous calculation of Peterson & Woods (see Turner 1992).

Table C1. Equilibrium distance ($r_{\mathrm{S-O}}$), harmonic frequency (ν), rotational constant (B_e), and the dipole moment (μ) for the cation SO$^+$($^2\Pi$).

Method	$r_{\mathrm{S-O}}$ (Å)	ν (cm^{-1})	B_e (MHz)	μ (Debye)
CCSD(T)-F12/RI/cc-pVQZ-F12^a	1.4256	1323.19	23297.53460	2.016
Exp. (ref)	1.4245	1306.78	23341.60095	—-

(a) For the correlation and coulomb fitting the augmented aug-cc-pV5Z was used.

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