

Rotational rate coefficients of $\text{SN}^+(\text{}^1\Sigma)$ by collision with He

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ABSTRACT

The SN^+ ion has been detected for the first time in the interstellar medium (ISM) very recently. The analysis of the physical–chemical conditions of the regions where this molecule has been observed requires accurate collisional rates coefficients with the most common colliders in the ISM. The main goals of this work are to study the collision of SN^+ with He and report the collisional rate coefficients for this system. A three-dimensional potential energy surface was developed from *ab initio* energies at the CCSD(T)/aug-cc-pV5Z level of theory fitted using a procedure based on the reproducing kernel Hilbert space approach. Close coupling calculations were performed, and the rate coefficients for the lowest 27 rotational states of SN^+ are reported. Furthermore, the rate coefficients considering the hyperfine transitions are also explored.

Key words: astrochemistry – molecular data – molecular processes – scattering – ISM: molecules.

1 INTRODUCTION

Very recently, Cernicharo et al. (2018) reported the first observation of the SN^+ cation in the interstellar medium (ISM). Its constituent elements, sulfur and nitrogen, are of interest to the astronomical community. Severe sulphur depletion in dark clouds has prompted an effort for the identification of new species (Agúndez et al. 2018). Nitrogen abundance is better understood but can only be determined indirectly, as N_2 is not directly observable (Daniel, Cernicharo & Dubernet 2006; Pagani, Bourgoïn & Lique 2012; Cernicharo et al. 2018). Both elements, but especially nitrogen, appear critical for the development of life (Fraústo da Silva & Williams 2001). The number of observed bearers of the two atoms is very limited. Therefore, the SN^+ molecule could be a good tracer of physical–chemical conditions in dark clouds of different evolutionary stages (Cernicharo et al. 2018).

The SN^+ ion is formed in the ISM mostly by the reactions of N with SO^+ and SH^+ . Its destruction processes include reactions with neutral O, N, and C, and dissociative recombination with electrons (Wakelam et al. 2012; Cernicharo et al. 2018). Collisions of SN^+ with the most common components of the ISM (e.g. He, H_2 , and H) have, to our knowledge, not been studied.

The collisional rates of observed species, such as SN^+ , with He and H_2 , and the Einstein coefficients are required for determining density, temperature, and molecular abundance in typical molecular clouds by non-local thermal equilibrium (non-LTE) models. The Einstein coefficients are usually known, but this is not the case with the collisional rates. In the absence of any collisional rate coefficients for a molecule, LTE conditions should be considered. The molecules are in LTE when the local gas density is larger than a critical value. However, the ISM has low density, and the collisions are rare. Therefore, the LTE is not a good approximation. If only the rates for the collision with He are available, they are used to model those with H_2 (Schöier et al. 2005; Wernli et al. 2006; Lique et al. 2008; Denis-Alpizar et al. 2013; Hernández Vera et al. 2017; Yang et al. 2018). In the case that any data for a given molecule is available, astronomers estimate the rates from those of isoelectronic species. Such last estimation was done by Cernicharo et al. (2018) for SN^+ . The rates coefficients for SN^+ in collision by He were scaled by a factor of 5 from those reported for $\text{CS} + \text{He}$ (Lique & Spielfiedel 2007). However, the use of the rates for a neutral system to model the collision with an ion deserves to be evaluated. Furthermore, as in the identification of SN^+ the hyperfine structure of the $j = 2 \rightarrow 1$ transitions was observed, the determination of the hyperfine rate coefficients for the collision processes would also be valuable.

The use of new observational facilities, e.g. ALMA, has increased the number of molecules observed in the ISM in the last years and

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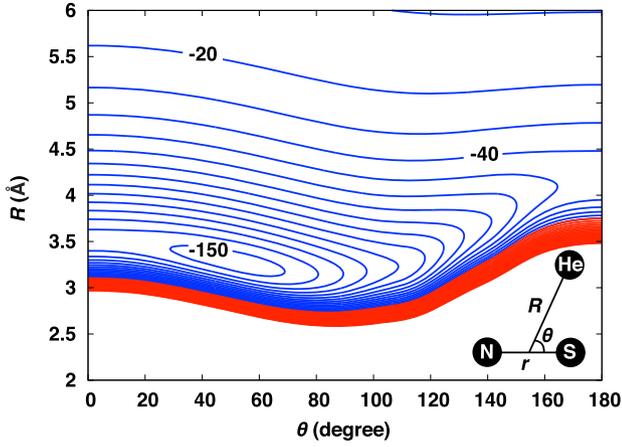


Figure 1. Contour plot of the PES at $r = 1.44 \text{ \AA}$. Negative lines in step of 10 cm^{-1} represent the positive potential energy.

therefore the requirement of collisional rates of such systems with He and H_2 . Even though the theory of scattering was developed in the sixties (Arthurs & Dalgarno 1960), the computational cost of developing an accurate potential energy surface (PES), and performing close coupling calculations, particularly for collision with H_2 , has meant that there are still many molecular collisions to be studied. In the case of ionic systems, considering the collision with He instead of H_2 reduces the dimensionality of the interaction and also the analysis of the probability of formation of chemical bond and reaction. For these reasons, the ion-He interactions have received large attention in last years (Walker et al. 2016; Bop et al. 2017a,b; Werfelli et al. 2017; Bop, Hammami & Faye 2017c; Tchakoua, Motapon & Nsangou 2018).

The main goals of this work are to study the collision of SN^+ with He and report the rotational and hyperfine rate coefficients for this system. This article is organized as follows: in the next section, the method used in the development of the PES as well as in the dynamics are presented. In Section 3, the results are discussed, while Section 4 summarizes this work.

2 METHODOLOGY

2.1 Potential energy surface

A three-dimensional PES for SN^+ in collision with He was developed from *ab initio* energies computed at the CCSD(T) method considering the aug-cc-pV5Z basis set. The *ab initio* calculations were performed using the Molpro package (Werner et al. 2012). The basis set superposition errors were corrected with the counterpoise method of Boys & Bernardi (1970).

The spatial Jacobi coordinates (r, R, θ) were employed for describing the geometry orientation of the $\text{SN}^+ + \text{He}$ system, see Fig. 1. The grid includes six values of r from 1.05 \AA to 1.65 \AA (1.44 \AA was found to be the equilibrium distance of SN^+), 28 values of R in the interval $[1.5, 16] \text{ \AA}$, and 11 angular configuration in the interval between 0 and 180 degree. In total 1848 *ab initio* energies were computed.

The analytical PES was obtained, using the reproducing kernel Hilbert space method described by Ho & Rabitz (1996), as

$$V(\mathbf{x}) = \sum_{k=1}^N \alpha_k Q(\mathbf{x}_k, \mathbf{x}), \quad (1)$$

where N is the number of *ab initio* points, \mathbf{x} is the vector of the internal coordinates, \mathbf{x}_k is the coordinate of the k th *ab initio* energy, and $Q(\mathbf{x}_k, \mathbf{x})$ is the multiplication of the one-dimensional kernels

$$Q(\mathbf{x}_k, \mathbf{x}) = q^{2,3}(R_k, R)q^{2,3}(r_k, r)q^2(z_k, z), \quad (2)$$

where $z = \frac{1 - \cos\theta}{2}$. The α_k coefficients are found by solving the linear system $\mathbf{V}(\mathbf{x}_i) = \alpha \mathbf{Q}(\mathbf{x}_i, \mathbf{x}_j)$, where i and j label the different geometrical configuration of the grid. The $q^{2,3}(R_k, R)$ kernel guarantees the correct R^{-4} large range dependence (Soldán & Hutson 2000). This methodology has been used recently for studying other ion-atom systems like $\text{AlO}^+ + \text{He}$, $\text{CF}^+ + \text{He}$, and $\text{SN}^- + \text{H}$ (Ajili et al. 2016; Denis-Alpizar, Inostroza & Castro Palacio 2018a; Denis-Alpizar et al. 2018b).

2.2 Dynamics

The PES previously described was employed for studying the dynamics of the collision of SN^+ with He. The close coupling equations were solved in the space-fixed frame. It is worth noting that an excellent agreement between the results of this method and experimental data has been found for several collisions, e.g. $\text{O}_2 - \text{H}_2$ (Lique et al. 2014), $\text{CO} - \text{H}_2$ (Yang et al. 2015), $\text{CN} - \text{H}_2$ (Yang et al. 2016), and $\text{CO} - \text{Ar}$ (Mertens et al. 2017). The NEWMAT code (Stoecklin, Voronin & Rayez 2002) was employed for the calculations. The log-derivative propagator was used and the minimum propagation distance employed was $50 a_0$. The vibration of the SN^+ molecule is treated by solving the exact diatomic equations employing the *ab initio* diatomic potential and a finite basis representation of imaginary exponential (Colbert & Miller 1992). The rovibrational wave functions are then evaluated along a Gauss-Hermite grid.

The convergence of the quenching inelastic cross-section was checked in function of the total angular momentum J . The state-to-state rate coefficients were computed by a Boltzmann averaging the corresponding cross-sections $\sigma_{j \rightarrow j'}$ at a given temperature T

$$k_{j \rightarrow j'}(T) = \sqrt{\frac{8}{\pi \mu k_B^3 T^3}} \int_0^\infty \sigma_{j \rightarrow j'}(E_c) E_c e^{-\frac{E_c}{k_B T}} dE_c, \quad (3)$$

where E_c is the collision energy, k_B is the Boltzmann constant, and j , and j' are the initial and final rotational quantum numbers.

The nuclear spin of nitrogen ($I = 1$) can be included in the calculation using the infinite-order-sudden (IOS) approximation for a $^1\Sigma$ molecule for determining the hyperfine rate coefficients (Faure & Lique 2012). Briefly, rate coefficients from the hyperfine level F (F varies from $|I - j|$ to $|I + j|$) can be computed using the spin-free rotational close coupling rate coefficients. In the IOS approximation, the inelastic rate from a given rotational state j can be obtained from the rates calculated for the initial rotational state $j = 0$ by

$$k_{j \rightarrow j'}^{\text{ios}}(T) = (2j' + 1) \sum_L \begin{pmatrix} j' & j & L \\ 0 & 0 & 0 \end{pmatrix}^2 k_{0 \rightarrow L}(T), \quad (4)$$

where the $(::)$ is a Wigner 3- j symbol and the $k_{0 \rightarrow L}$ was considered in this work as the fundamental close coupling rates as it was suggested by Faure & Lique (2012) following the work of Goldflam, Kouri & Green (1977). The hyperfine rate coefficients can be obtained by

$$k_{jF \rightarrow j'F'}^{\text{ios}}(T) = (2j + 1)(2j' + 1)(2F' + 1) \sum_L \begin{pmatrix} j' & j & L \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} j' & j & L \\ F' & F & I \end{matrix} \right\}^2 k_{0 \rightarrow L}(T) \quad (5)$$

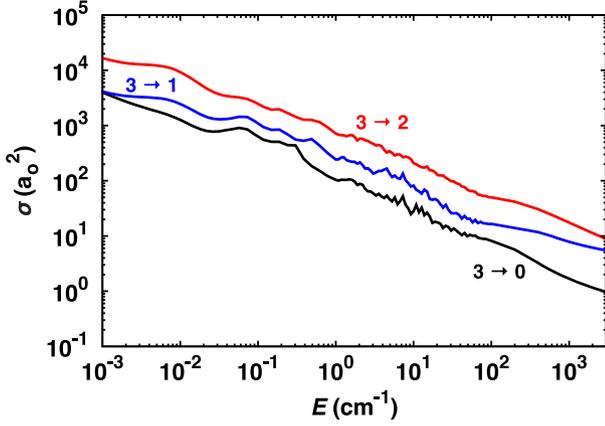


Figure 2. De-excitation cross-sections from the initial state $\nu = 0, j = 3$. Each line is labelled as $j_i \rightarrow j_f$.

where the $\{::\}$ is the 6- j symbol. Finally, the hyperfine rates are then computed as

$$k_{jF \rightarrow j'F'}^{\text{IOS}}(T) = \frac{k_{jF \rightarrow j'F'}^{\text{ios}}(T)}{k_{j \rightarrow j'}^{\text{ios}}(T)} k_{j \rightarrow j'}^{\text{CC}}(T), \quad (6)$$

where $k_{j \rightarrow j'}^{\text{CC}}$ is the rotational close coupling rate coefficients computed in equation (3). This method was recently applied to the collisions $\text{CF}^+ + \text{He}$ (Denis-Alpizar et al. 2018a) and $\text{AlO}^+ + \text{He}$ (Denis-Alpizar et al. 2018b) for obtaining the state-to-state hyperfine rates coefficients.

3 RESULTS

The interaction *ab initio* energies were fitted to an analytical function as it was described in the previous section. A contour plot of the surface is shown in Fig. 1. The global minimum of the interaction PES, namely -154.8 cm^{-1} , at $r_e = 1.44 \text{ \AA}$ was found at the bend configuration $R = 3.26 \text{ \AA}$ and $\theta = 53.5^\circ$. This complex is more bound than $\text{CS} + \text{He}$ (Lique, Spielfiedel & Cernicharo 2006), for which the global minimum, namely -21.8 cm^{-1} , is seven times lower than for $\text{SN}^+ + \text{He}$.

The first use of this PES was to compute the rotational cross-sections within the vibrational states $\nu = 0$ of SN^+ in the interval $(10^{-3} - 3000) \text{ cm}^{-1}$. As SN^+ has a small rotational constant, $B_e = 0.8319 \text{ cm}^{-1}$ (Karna & Grein 1986), many rotational channels should be considered in the calculations. Two sets of the cross-sections from $j = 5$ and 20, using two different bases including 32 and 40 rotational states in each of the two lower vibrational levels of SN^+ , were compared. The differences between both sets at 10, 100, and 500 cm^{-1} were lower than 0.5 per cent for all de-excitation transitions. Therefore, the basis used in this work includes 32 rotational states for the two lower vibrational levels of SN^+ , which is enough for reaching convergence. Fig. 2 shows the de-excitation cross-section from $j = 3$. The typical shape and Feshbach resonances can be seen in this figure at energies lower than 100 cm^{-1} which are associated with the van der Waals well allowing the formation of quasi-bound states.

The de-excitation rate coefficients from the initial states $j = 4$ and 5 are shown in Fig. 3. The rates for the $\text{CS} + \text{He}$ collision scaled by a factor of 5 are also included in this figure. The scaled approximation does not model the rates for the $\text{SN}^+ + \text{He}$ collision.

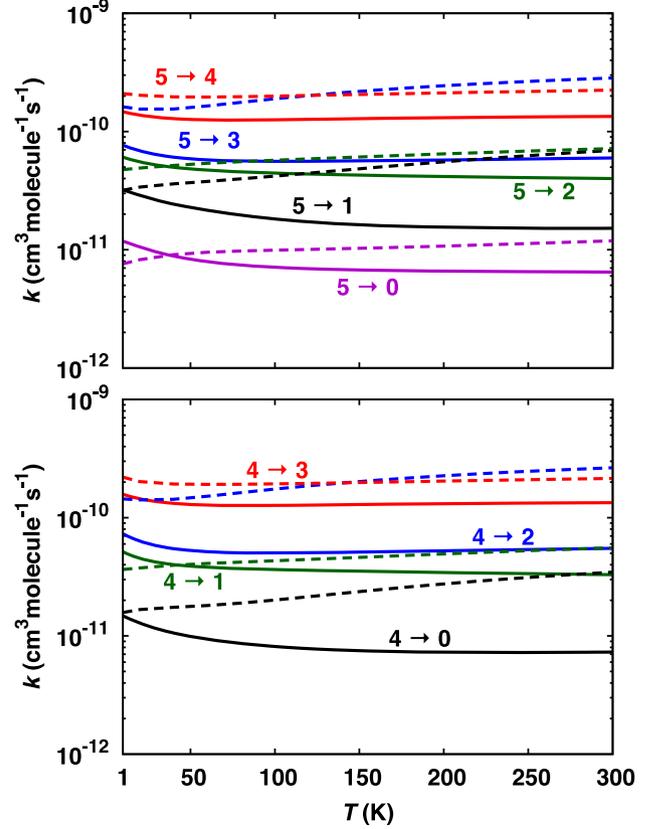


Figure 3. Rotational rate coefficient for the initial state $j = 4$ and 5 within the vibrational $\nu = 0$ level. The scaled rate coefficients from the $\text{CS} + \text{He}$ collision are also included (dashed lines). Each line is labeled as $j_i \rightarrow j_f$.

Such disagreement is not surprising due to the differences in the PES of both systems. The cross-sections, and consequently the rate coefficients, are very sensitive to the large range of the PES. In the case of neutral systems, such as $\text{CS} + \text{He}$, the asymptotic behavior of the surface is R^{-6} , while for the ion-atom systems, such as SN^+ , such behavior is R^{-4} . The rotational rates up to $j = 27$ in the ground vibrational states from 10 to 305 K can be found in the Supplementary Materials.

An extra set of close coupling calculations were performed for $j = 0$. In this case, the convergence was checked for the total inelastic cross-section. With these rates, the equations (4) and (5), can be employed. In Table 1, the IOS state-to-state hyperfine rate coefficients at several temperatures are showed. The use of the IOS method for the $\text{HCN} + \text{H}_2$ and $\text{CN} + \text{H}_2$ systems was found to be in good agreement with the ‘exact recoupling method’ (Faure & Lique 2012). In Supplementary Material can be found the IOS hyperfine rate coefficients for the lower rotational states of SN^+ in collision with He. It is worth mentioning that for the transitions among the levels $j = 1, F = 0$, and $j', F' = j$ the IOS rates are strictly 0 due to the restriction of equation (5). In the case of $\text{HCN} + \text{H}_2$, Faure & Lique (2012) found that the exact recoupling method also shows very small rate coefficients for such transitions. The new data reported in this work would be valuable for the interpretation of the physical-chemical conditions of the ISM regions where SN^+ is detected.

The rotational rates decrease with the increment of Δj with the $\Delta j = 1$ propensity rule. This behavior is typical of collisions of atoms with different masses. Recently, the same behavior was found for

Table 1. Hyperfine IOS rate coefficients ($10^{-11} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$) of SN^+ in collision with He at selected temperatures. Full table of rotational and hyperfine rate coefficients for this system can be found in the Supplementary Materials.

j_i	F_i	j_f	F_f	10 K	50 K	100 K	150 K	300 K
1	0	0	1	9.01	6.77	6.80	7.05	7.15
1	0	1	2	3.47	4.33	5.58	6.61	7.45
1	1	0	1	9.01	6.77	6.80	7.05	7.15
1	1	1	2	2.60	3.25	4.18	4.96	5.59
1	2	0	1	9.01	6.77	6.80	7.05	7.15
1	2	1	0	0.69	0.87	1.12	1.32	1.49
1	2	1	1	1.56	1.95	2.51	2.97	3.35
2	1	0	1	2.94	1.87	2.03	2.25	2.66
2	1	1	0	7.49	4.78	4.58	4.68	4.92
2	1	1	1	5.61	3.59	3.44	3.51	3.69
2	1	1	2	1.95	3.06	3.25	3.30	3.20
2	1	2	2	1.44	1.67	2.05	2.37	2.79
2	1	2	3	0.59	2.23	2.45	2.51	2.61
2	2	0	1	2.94	1.87	2.03	2.25	2.66
2	2	1	1	10.63	7.40	7.20	7.35	7.63
2	2	1	2	4.42	4.03	4.08	4.15	4.19
2	2	2	1	0.87	1.00	1.23	1.42	1.68
2	2	2	3	1.22	2.28	2.63	2.87	3.19
2	3	0	1	2.94	1.87	2.03	2.25	2.66
2	3	1	0	0.38	0.67	0.72	0.73	0.70
2	3	1	1	0.75	1.34	1.44	1.46	1.41
2	3	1	2	13.92	9.41	9.12	9.31	9.70
2	3	2	1	0.25	0.95	1.05	1.08	1.12
2	3	2	2	0.87	1.63	1.88	2.05	2.28

the collision of AlO^+ with He (Denis-Alpizar et al. 2018b). In the case of hyperfine transitions, a clear $\Delta j = \Delta F$ propensity rule can be seen in Table 1, also Faure & Lique (2012) pointed such propensity rule in the case of the $\text{HCN}+\text{H}_2$ system.

4 SUMMARY

A three-dimensional PES for the SN^++He system at the CCSD(T)/aug-cc-pV5Z level of theory was developed. This surface was employed to compute the close-coupling cross-sections and rate coefficients. These rates were compared with those scaled from the $\text{CS}+\text{He}$ collision. The latter approximation showed to be inaccurate.

Even though the rate coefficients of SN^+ in collision with He are provided in this work, it is worth noting the mass scaling approximation (Schöier et al. 2005) is not valid for modelling of the collision of SN^+ with ortho- H_2 . For the case of the collision with para- H_2 , such approximations should be considered carefully (Walker et al. 2016). A future study of the collision of SN^++H_2 would be valuable.

Finally, the first set of rotational and hyperfine rate coefficients for the lower rotational states of SN^+ in collision with He was reported. The propensity rule for $\Delta j = \Delta F$ was observed. The data here reported is expected to be useful for the astronomy community for the study of the region where SN^+ is observed.

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REFERENCES

- Agúndez M., Marcelino N., Cernicharo J., Tafalla M., 2018, *A&A*, 611, L1
- Ajili Y., Trabelsi T., Denis-Alpizar O., Stoecklin T., Császár A., Al-Mogren M. M., Francisco J., Hochlaf M., 2016, *Phys. Rev. A*, 93, 052514
- Arthurs A. M., Dalgarno A., 1960, *Proc. R. Soc. A*, 256, 540
- Bop C. T., Trabelsi T., Hammami K., Mogren Al Mogren M., Lique F., Hochlaf M., 2017a, *J. Chem. Phys.*, 147, 124301
- Bop C. T., Hammami K., Niane A., Faye N., Jaïdane N., 2017b, *MNRAS*, 465, 1137
- Bop C. T., Hammami K., Faye N. A. B., 2017c, *MNRAS*, 470, 2911
- Boys S. F., Bernardi F., 1970, *Mol. Phys.*, 19, 553
- Cernicharo J. et al., 2018, *ApJ*, 853, L22
- Colbert D. T., Miller W. H., 1992, *J. Chem. Phys.*, 96, 1982
- Daniel F., Cernicharo J., Dubernet M.-L., 2006, *ApJ*, 648, 461
- Denis-Alpizar O., Stoecklin T., Halvick P., Dubernet M.-L., 2013, *J. Chem. Phys.*, 139, 204304
- Denis-Alpizar O., Inostroza N., Castro Palacio J. C., 2018a, *MNRAS*, 473, 1438
- Denis-Alpizar O., Trabelsi T., Hochlaf M., Stoecklin T., 2018b, *MNRAS*, 475, 783
- Faure A., Lique F., 2012, *MNRAS*, 425, 740
- Fraústo da Silva J., Williams R., 2001, *The biological Chemistry of the elements: The inorganic chemistry of life*. Oxford Univ. Press Inc., New York, USA
- Goldflam R., Kouri D. J., Green S., 1977, *J. Chem. Phys.*, 67, 5661
- Hernández Vera M., Lique F., Dumouchel F., Hily-Blant P., Faure A., 2017, *MNRAS*, 468, 1084
- Ho T. S., Rabitz H., 1996, *J. Phys. Chem.*, 104, 2584
- Karna S., Grein F., 1986, *Chem. Phys.*, 109, 35
- Lique F., Spielfiedel A., 2007, *A&A*, 462, 1179
- Lique F., Spielfiedel A., Cernicharo J., 2006, *A&A*, 451, 1125
- Lique F., Tobała R., Klos J., Feautrier N., Spielfiedel A., Vincent L. F. M., Chafański G., Alexander M. H., 2008, *A&A*, 478, 567
- Lique F., Kalugina Y., Chefdeville S., van de Meerakker S. Y. T., Costes M., Naulin C., 2014, *A&A*, 567, A22
- Mertens L. A., Labiad H., Denis-Alpizar O., Fournier M., Carty D., Le Picard S. D., Stoecklin T., Sims I. R., 2017, *Chem. Phys. Lett.*, 683, 521
- Pagani L., Bourgoïn A., Lique F., 2012, *A&A*, 548, L4
- Schöier F. L., van der Tak F. F. S., van Dishoeck E. F., Black J. H., 2005, *A&A*, 432, 369
- Soldán P., Hutson J. M., 2000, *J. Chem. Phys.*, 112, 4415
- Stoecklin T., Voronin A., Rayez J. C., 2002, *Phys. Rev. A*, 66, 042703
- Tchakoua T., Motapon O., Nsangou M., 2018, *J. Phys. B*, 51, 045202
- Wakelam V. et al., 2012, *ApJS*, 199, 21
- Walker K. M., Dumouchel F., Lique F., Dawes R., 2016, *J. Chem. Phys.*, 145, 024314
- Werfelli G., Balança C., Stoecklin T., Kerkeni B., Feautrier N., 2017, *MNRAS*, 468, 2582
- Werner H.-J., Knowles P. J., Knizia G., Manby F. R., Schütz M., 2012, *WIREs Comput. Mol. Sci.*, 2, 242
- Wernli M., Valiron P., Faure A., Wiesenfeld L., Jankowski P., Szalewicz K., 2006, *A&A*, 446, 367
- Yang B., Zhang P., Wang X., Stancil P. C., Bowman J. M., Balakrishnan N., Forrey R. C., 2015, *Nature Commun.*, 6, 6629
- Yang B., Wang X. H., Stancil P. C., Bowman J. M., Balakrishnan N., Forrey R. C., 2016, *J. Chem. Phys.*, 145, 224307
- Yang B. et al., 2018, *J. Phys. Chem. A*, 122, 1511

SUPPORTING INFORMATION

Supplementary data are available at [MNRAS](#) online.

Table 1. Hyperfine IOS rate coefficients ($10^{-11}\text{cm}^3\text{molecules}^{-1}\text{s}^{-1}$) of SN⁺ in collision with He at selected temperatures.

Rotational rate coefficients for the SN⁺–He collision

Hyperfine rate coefficients for the SN⁺–He collision

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