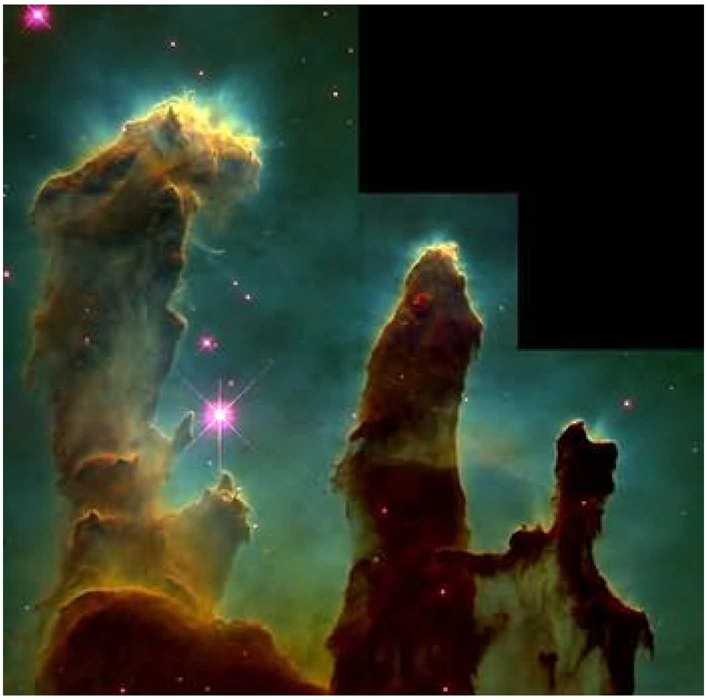
Chem3105
Physical Chemistry Research Project

Interstellar Clouds



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Abstract

This report presents energy and kinetic data for gas-phase sodium-bonded complexes found in interstellar clouds. CP-dG2thaw calculations, which are a high level of theory specifically designed for the computation of complexes that involve metal cations, were used to find the bond dissociations energies for a number of complexes containing a sodium cation. The report also details collisional rate coefficients using the Su and Chesnavich method, and radiative rate coefficients using the method by Herbst, presenting details about the importance of the reactions studied in regards to Na^+ cation removal in outer space.

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1 Introduction

There has been an increase in the interest of sodium compounds recently, due to its importance in organic and biochemistry in the gas-phase. The detection of sodium in interstellar clouds makes the investigation of rate coefficients at low temperatures particularly interesting.

Interstellar clouds are composed of a number of gas-phase complexes at very low densities. The temperature observed in these interstellar clouds ranges from around 10K to above 300K. Due to the low concentrations, there is only expected to be about one collision per day for a given ligand. Because of this low amount of collisions, the primary process of energy dissipation for the gaseous complexes is radiative emission. The competition between dissociation and radiative emission leads us to the question of which ligands can be considered as a viable means of sodium cation capture.

2 Background Theory

2.1 Bond Dissociation Energies

2.1.1 Binding in Gas-Phase Complexes of Sodium Ions

In order to predict where possible binding sites of sodium to a ligand may occur, knowledge of accurate binding interactions is required. This allows the prediction of bond dissociation energies.

2.1.2 CP-dG2thaw

In determining the metal ligand binding energies, the B3-LYP/6-311+G** procedure was used. This procedure is based around a widely used Gaussian-2 (G2)[1] model chemistry method. A large number of computational chemistry studies use this model to determine thermochemical information for many small main-group compounds that are difficult to generate experimentally.

The G2 method expresses total energy as:

$$\begin{gathered} E_0(X) = (E_{MP2} + E_{QCISD(T)} - 2E_{MP4SDTQ})B1G \\ + (E_{MP4SDTQ} - E_{MP2})B2G \\ + (E_{MP4SDTQ} - E_{MP2})B3G \\ + (E_{MP2)})B4G \\ + ZPE + HLC, \end{gathered}$$

where the E_{MP2}, $E_{MP4DSTQ}$, $E_{QCISD(T)}$ are the single point total energies of the respective indicated level of correlation of the B*n*G basis set, ZPE is the zero-point vibrational energy and HLC is a higher-level correction used to reduce the deficiencies in the finite-sized basis sets.

The single point calculations correlate only the valence electrons (frozen core) with the basis sets are respectively B1G = 6-311G**, B2G = 6-311G**, B3G = 6-311(2df,p) and B4G = 6-311+G(3df,2p). All the single point energies use a geometry optimised at a lower level of theory (MP2/6031G*).

The ultimate purpose is to calculate an approximation of a total energy from a very high level of theory (QCISD(T)/6-311+G(3DF,2P) in a shorter CPU time than the large calculation would require.

Although the G2 method is quite reliable in most of its applications (±8 KJ mol^{-1}) it has some shortcomings such as calculations on compounds containing main-group metals like sodium. To counter this, a variant to the G2 theory was developed by Dr Petrie called CP-dG2thaw [2], which aims at addressing the shortcomings of the standard G2 metal-containing ions.

The CP –dG2thaw total energy for am metal obtaining ion MX^+ is

$$
\begin{gathered}
E_0(X) = (E_{MP2} + E_{QCISD(T)} - 2E_{MP4SDTQ})B1G \\
+ (E_{MP4SDTQ} - E_{MP2})B2G \\
+ (E_{MP4SDTQ} - E_{MP2})B3G \\
+ (E_{MP2)})B4G \\
+ ZPE + CP(MX^+),
\end{gathered}
$$

in which $CP(MX^+) = \{[E_{MP2}(M^+) - E_{MP@}(M^+Bq_X)] + [E_{MP2}(X) - E_{MP2}(Xbq_M)]\}B4G$.

The main differences between the standard G2 model and the CP-dG2thaw method are:

(1) all single point calculations include the metal atom’s ‘inner valence’ electrons (the 2s and 2p electrons for sodium) amongst those correlated, **thawing** out the ‘frozen-core’ of the G2 method

(2) the basis set, B4G, for sodium , magnesium and aluminium is partially decontracted from the standard 6-311+G(3df,2p) basis set. In other atoms the B*n*G basis sets are the same as defined in the G2 method.

(3) The CP–dG2thaw does not have a ‘Higher Level Correction” but instead a counterpoise correction $CP(MX^+)$ is used at the MP2/B4G level of theory for the basis set superposition error in the M^+-X bonding interaction. This correction determines the differences in total energy for the metal ion and the ligand depending on the presence (Bq, representing one or more ‘ghost atoms’) or absence of the other fragment’s basis functions.

The determination of the total energy CP–dG2thaw requires 10 chemical calculations:

(1) Geometry optimisation in which the B3-LYP/6-311+G** optimisation is used.

(2) Determination of the zero-point vibrational energy using the B3-LYP/6-311+G**.

(3-5) Single point total energy calculations using the respective B*n*G basis sets at a sufficiently high level of theory to determine all the energies which are required at that basis set.

(6) A single point calculation for MP2/B4G

(7-10) MP2/B4G calculations on the fragments M^+, M^+Bq_X, X and Xbq_M with atom positions identical to those within the optimised geometry MX^+. (note that $Bq_{\backslash X}$, Bq_M are ‘ghost atom’ structures: the basis functions are those applying to the full molecular ion MX^+, but either X or M^+ is absent.

The Bond Dissociation Energy is then calculated using the formula,

$$\mathrm{BDE}(\mathrm{M}^{+}\text{-}\mathrm{X}) = \mathrm{E}(\mathrm{M}^{+}) + \mathrm{E}(\mathrm{X}) - \mathrm{E}(\mathrm{MX}^{+})$$

It can be seen that the total energies for the separated M^+ ion and the ligand must also be calculated.

2.2 Kinetics

2.2.1 Collisional Rate Coefficient

The collisional rate coefficient is the coefficient of proportionality which describes the relationship between the rate of a step in a chemical reaction and the concentrations of the reactants consumed after a collision has occurred.

Su and Chesnavich [3] have devised a method that is a reliable way to determine collisional rate coefficients at low temperatures. By treating the ion as a point charge and the polar molecule as a two dimensional rigid rod, the interaction potential can be found using Equation 1:

$$V(r,\theta) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2}\cos\theta$$

Equation 1

Where: α is the polarizability,

μ_D is the dipole moment of the neutral,

r is the distance between the ion and the centre of mass of the neutral,

θ is the angle between the dipole and r

q is the charge of an electron.

From this, the thermal capture rate coefficient can be determined using the expression:

$$k_{cap}(T) = \frac{1}{2Ik_B T(2\pi\mu k_B T)^{3/2}} \int Xr\{p,q\} d\gamma_1 d\gamma_2 dL dJ 2\tau d\tau \times e^{-E/k} B^T dE$$

Equation 2

A FORTRAN program named COLRATE [4] that utilises the above method can be used to find the collisional rate coefficients.

2.2.2 Radiative Association Rate Coefficients

The radiative association rate coefficient is related to the rate at which a complex can radiate sufficient energy to prevent dissociation back into reactants. Herbst [5] derived Equation 3, involving a function of dissociation energies ($N_{vr}(D_0)$) shown below.

$$k_{RA} = \frac{h^3 T^{-1/2}}{(2\pi\mu)^{3/2} k^{1/2}} g^{en}_{AB^*} \frac{N_{vr}(D_0) k_r}{q_A^{\text{int}} q_B^{\text{int}}}$$

Equation 3

Where: k_{RA} is the radiative association coefficient,
h = Planck's constant,
T = Temperature (K),
μ = Reduced mass,
k = Boltzmann's constant.

For bond energies in excess of ~1eV, we are able to utilize the formula of Whitten and Rabinowitch which can be written as:

$$N_{vr}(D_0) = \frac{q^{rot}(\tilde{D}_0 + \tilde{E}_z)^{s+\frac{r}{2}-1}}{(\tilde{k}T)^{\frac{r}{2}} hc\sigma\Gamma(s+\frac{r}{2})\Pi_i \tilde{\upsilon}_i}$$

Equation 4

Here, D_0 = Dissociation Energy,
E_z = Zero=point energy (AB),
q^{rot} = classical rotation partition function,
σ = symmetry number,
v_i = harmonic frequencies,
s = number of AB* vibrational modes,
r = number of AB* rotational degrees of freedom,
Γ = Gamma function,
c = speed of light.

All quantities under the tilde symbol are measured in wavenumber units (cm^{-1}). The factor $q^{rot}/(kT)^{r/2}$ is independent of temperature (see below), and both rigid body and nonrigid rotations can be included in q^{rot}. The internal partition functions for A and B in relation to Equation 3 can normally be restricted to rigid-body rotational degrees of freedom, and so q_A^{int} can be written as:

$$q_A^{\text{int}} = g_A^{en} q_A^{rot}$$

Equation 5

Where, g_A^{en} = electronic-nuclear spin degeneracy = 1. If A is a non-linear molecule and the rotational energy can be treated as a classical, continuous variable we can use the method derived by Townes and Schawlow,

$$q_A^{rot} = \frac{\pi^{1/2}}{\sigma}(\tilde{k}T)^{3/2}(\tilde{A}\tilde{B}\tilde{C})^{-1/2}$$

Equation 6

Where A,B and C are the rotation constants. If A is a linear molecule than we are able to use the simplified equation:

$$q_A^{rot} = \frac{\tilde{k}T}{\sigma \tilde{B}}$$

Equation 7

The rate co-efficient has been estimated by Herbst to be:

$$k_r(s^{-1}) \approx 10^2 n$$

Equation 8

Where n = number of excited infrared active vibrational quanta in AB* = 1.

3 Computational Procedure

The geometry of a number of ligands was generated in MOLDEN [6], as well as the ligand bonded to a Na^+ ion. Different conformations of the complex were generated, as each has a different binding energy and different vibrational frequencies. The ligands used are listed in Table 1. These geometries were then optimised using Gaussian 98 [7].

The optimised geometries were then used to calculate the binding energies, radiative frequencies, and other details about the ligands and their respective complexes, as required for the CP-dG2thaw level of theory, the program COLRATE, and the radiative association theory, as described above.

The results from Gaussian were used to calculate binding energies between the ligands and Na^+ ions, according to CP-dG2thaw theory, the collision rates for the ligands and Na^+ ions in conditions such as those in interstellar clouds, and the rate of radiative loss of the excess energy.

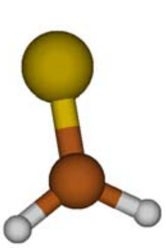
3.1 Table of Complexes

Name of Ligand	Structural Formula	Mass (amu)	Complex Formula	2^{nd} Complex Formula
Carbon Monoxide	CO	28.0104	$NaOC^+$	$NaCO^+$
Thioformaldehyde	CH_2S	46.0928	CH_2SNa^+	
Hydrogen Peroxide	HOOH	34.0146	$HONaOH^+$	
Hydroxylamine	NH_2OH	33.0298	NH_2OHNa^+ (1)	NH_2OHNa^+ (2)
Hydrazine	H_2NNH_2	32.045	$H_2NNaNH_2^+$	
Cyclopropenylidene	c-C_3H_2	38.0488	c-$C_3H_2Na^+$	
Vinyl Alcohol	H_2CCHOH	44.053	$H_2CCHOHNa^+$ (1)	$H_2CCHOHNa^+$ (2)
Ethylene Oxide	c-C_2H_4O	44.053	c-$C_2H_4ONa^+$	
Formic Acid	HCOOH	46.0256	$HOCHONa^+$	$NaHOCHO^+$
Cyanamide	NH_2CN	42.0402	H_2NCNNa^+	

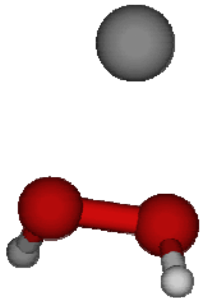
Table 1

3.2 Images of Complex Structures

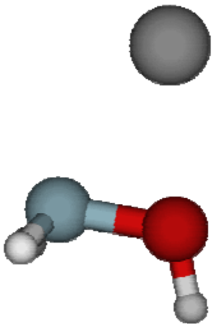
Screenshots from MOLDEN of the optimised geometries of some of the above complexes are included here for clarity.



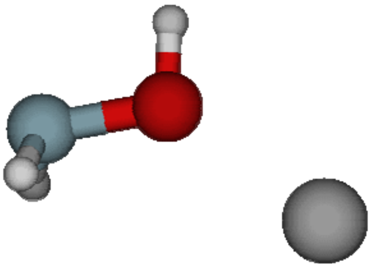
CH_2SNa^+



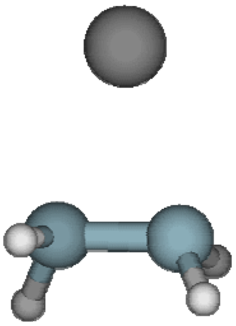
$HONaOH^+$



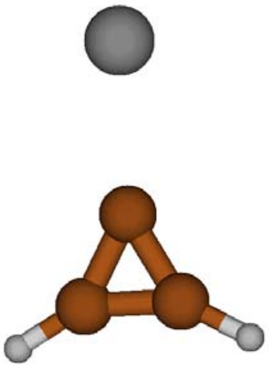
NH_2OHNa^+ (first orientation)



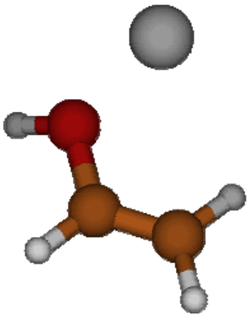
NH_2OHNa^+ (second orientation)



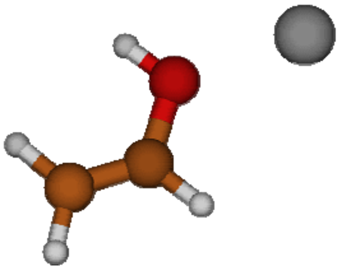
$H_2NNaNH_2^+$



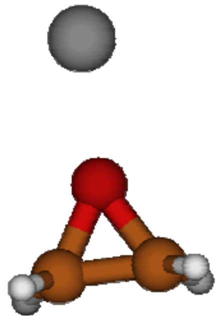
C_3H_2Na+



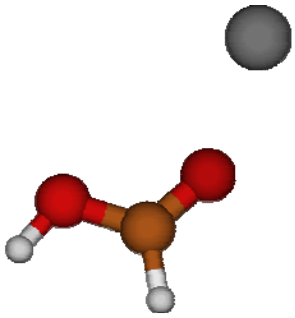
$H_2CCHOHNa^+$ (first orientation)



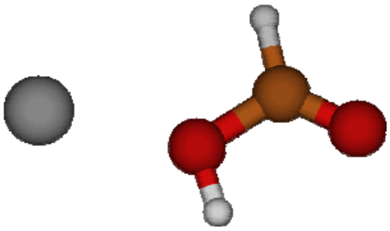
$H_2CCHOHNa^+$ (second orientation)



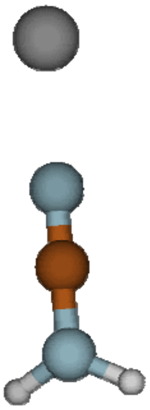
c-C2H4ONa+



$HOCHONa^+$



$NaHOCHO^+$



H_2NCNNa^+

4 Results

4.1 Bond Dissociation Energies

The following bond dissociation energies were all calculated using Gaussian 98 and the CP-dG2thaw method, as described above.

Ligand	Orientation	Bond Dissociation Energy [kJ/mol]
Carbon Monoxide	$NaOC^+$	26.99014
	$NaCO^+$	37.93086
Thioformaldehyde	CH_2SNa^+	71.51074
Hydrogen Peroxide	$HONaOH^+$	126.6392
Hydroxylamine	$NaNH_2OH^+$ (1)	108.4647
	$NaNH_2OH^+$ (2)	79.29115
Hydrazine	$H_2NNaNH_2^+$	118.9488
Cyclopropenylidene	$c\text{-}C_3H_2Na^+$	145.3939
Vinyl Alcohol	$H_2CCHOHNa^+$ (1)	90.48786
	$H_2CCHOHNa^+$ (2)	86.80638
Ethylene Oxide	$c\text{-}C_2H_4ONa^+$	241.6187
Formic Acid	$HOCHONa^+$	102.865
	$NaHOCHO^+$	46.90219
Cyanamide	H_2NCNNa^+	138.8868

Table 2

4.2 Data for Collision Rates

Desiring to simulate conditions in interstellar stars (where collisions happen once a day or so), a variety of temperatures ranging from 10 K to 300 K were used in calculating rate coefficients.

The program COLRATE required the following physical data about the ligand: polarizability, dipole moment, mass, and moment of inertia. The following information was required about the sodium ion: mass and charge. Where available, polarizability and dipole moment values were taken from the CRC handbook [8]. The moment of inertia of all ligands was calculated using the rotational frequencies given by Gaussian. Where dipole moment values were not available, they were also taken from the Gaussian output. The polarizability values from Gaussian were found to be a factor ~20 off published data for those that were found. Polarizability values that were not found were taken from Gaussian and scaled using a correction factor calculated from the difference between the Gaussian output for species which had published results and the published results.

4.2.1 Polarizabilities and dipole moments

Name of Ligand	Dipole Moment (debye)	Polarizability (angstroms^3)
Carbon Monoxide	0.10980[1]	1.95[1]
Thioformaldehyde	1.6491[1]	4.265[2]
Hydrogen Peroxide	1.573[1]	1.806[2]
Hydroxylamine	0.6791	2.24[2]
Hydrazine	2.0442[2]	2.84[2]
Cyclopropenylidene	3.4933[2]	4.20[2]
Vinyl Alcohol	1.015[2]	2.98[2]
Ethylene Oxide	1.89[1]	4.43[1]
Formic Acid	1.425[1]	3.4[1]
Cyanamide	4.28[1]	3.59[2]

Table 3

[1] CRC Handbook [8]

[2] Interpolation from Gaussian results [7]

4.3 Kinetics

4.3.1 Collisional Rate Coefficients

Complex	Collisional Rate coefficients at Temperature [K] (cm^{3}particle^{-1}s^{-1}E-9)							
	10K	20K	30K	50K	100K	150K	200K	300K
Carbon Monoxide	1.24	1.11	1.06	1.01	0.98	0.96	0.96	0.95
Thioformaldehyde	11.19	8.03	6.63	5.22	3.81	3.18	2.81	2.39
Hydrogen Peroxide	11.17	7.97	6.56	5.14	3.71	3.08	2.70	2.26
Hydroxylamine	5.03	3.65	3.03	2.42	1.822	1.60	1.46	1.32
Hydrazine	14.68	10.48	8.62	6.75	4.87	4.04	3.55	2.96
Cyclopropenylidene	24.08	17.14	14.07	10.99	7.89	6.51	5.69	4.72
Vinyl Alcohol	7.03	5.07	4.20	3.33	2.45	2.07	1.88	1.65
Ethylene Oxide	12.9	9.22	7.60	5.98	4.35	3.62	3.19	2.68
Formic Acid	9.69	6.95	5.74	4.52	3.30	2.76	2.44	2.09
Cyanamide	29.2	20.5	16.8	13.1	9.39	7.74	6.76	5.59

Table 4

4.3.2 Radiative Association Rate Coefficients

Ligand	Orientation	Radiative Rate coefficients at Temperature [K] ($cm^3s^{-1}particle^{-1}$)							
		10K	20K	30K	50K	100 K	150 K	200 K	300 K
Carbon Monoxide	$NaOC^+$	3.55 E-19	1.25 E-19	6.83 E-20	3.17 E-20	1.12 E-20	6.11 E-21	3.97 E-21	2.16 E-21
	$NaCO^+$	5.08 E-19	1.80 E-19	9.78 E-20	4.55 E-20	1.61 E-20	8.75 E-21	5.68 E-21	3.09 E-21
Thioformaldehyde	CH_2SNa^+	6.42 E-15	1.61 E-15	7.14 E-16	2.57 E-16	6.42 E-17	2.85 E-17	1.61 E-17	7.14 E-18
Hydrogen Peroxide	$HONaOH^+$	5.50 E-14	1.38 E-14	6.12 E-15	2.20 E-15	5.50 E-16	2.45 E-16	1.38 E-16	6.12 E-17
Hydroxylamine	$NaNH_2OH^+$ (1)	1.23 E-13	3.07 E-14	1.36 E-14	4.91 E-15	1.23 E-15	5.45 E-16	3.07 E-16	1.36 E-16
	$NaNH_2OH^+$ (2)	4.98 E-14	1.24 E-14	5.53 E-15	1.99 E-15	4.98 E-16	2.21 E-16	1.24 E-16	5.53 E-17
Hydrazine	$H_2NNaNH_2^+$	3.92 E-13	9.81 E-14	4.36 E-14	1.57 E-14	3.92 E-15	1.74 E-15	9.81 E-16	4.36 E-16
Cyclopropenylidene	$c\text{-}C_3H_2Na^+$	8.39 E-13	2.10 E-13	9.33 E-14	3.36 E-14	8.39 E-15	3.73 E-15	2.10 E-15	9.33 E-16
Vinyl Alcohol	$H_2CCHOHNa^+$ (1)	2.05 E-11	5.14 E-12	2.28 E-12	8.22 E-13	2.05 E-13	9.13 E-14	5.14 E-14	2.28 E-14
	$H_2CCHOHNa^+$ (2)	1.01 E-11	2.53 E-12	1.13 E-12	4.05 E-13	1.01 E-13	4.50 E-14	2.53 E-14	1.13 E-14
Ethylene Oxide	$c\text{-}C_2H_4ONa^+$	9.44 E-12	2.36 E-12	1.05 E-12	3.78 E-13	9.44 E-14	4.20 E-14	2.36 E-14	1.05 E-14
Formic Acid	$HOCHONa^+$	1.84 E-13	4.60 E-14	2.05 E-14	7.36 E-15	1.84 E-15	8.18 E-16	4.60 E-16	2.05 E-16
	$NaHOCHO^+$	6.02 E-15	1.51 E-15	6.69 E-16	2.41 E-16	6.02 E-17	2.68 E-17	1.51 E-17	6.69 E-18
Cyanamide	H_2NCNNa^+	8.26 E-12	2.06 E-12	9.17 E-13	3.30 E-13	8.26 E-14	3.67 E-14	2.06 E-14	9.17 E-15

Table 5

5 Discussion

5.1 *COLRATE Results*

The results from COLRATE, using the Su and Chesnovich theory, indicate a steady trend in the temperature dependence of the collision rates of the Na^+ ions and the ligands studied. The values range from 10^{-8} to 10^{-9} $cm^3particle^{-1}s^{-1}$, with collision rates inversely proportional to some power of the temperature. These already low rates, combined with the miniscule concentration of reactants in interstellar clouds, allow little opportunity for reactions to take place.

5.2 *Radiative Association Rate Results*

The results of the theory presented by Herbst for the Na^+-ligand adducts are presented in Table 5. These results range from 10^{-11} to 10^{-21} $cm^3s^{-1}particle^{-1}$, which is significantly less than the collision rates for the respective Na^+-ligand reactions. From the formula used, there is a temperature dependence of $k \propto T^{-\frac{1}{2}}$. The results calculated show this. It is understandable that carbon monoxide has the slowest rates, as it has the least number of atoms and the least vibrational modes.

5.3 The Verdict

In the reaction: A + Na^+ → ANa^+ + hν, the rate determining step is obviously the radiative emission step, which has rates consistently more than 10 orders of magnitude smaller than the collision rates, for all ligands. This implies that upon collision, a stable compound is unlikely to be formed, as only ~ 1 in 10^{11} (in the case of thioformaldehyde at 10 K, for example) collisions result in the emission of excess energy, causing a stable compound to be formed. Thus, none of the compounds studied present important reactions in regards to Na^+ capture in interstellar clouds.

6 Conclusion

The ligands Carbon Monoxide, Thioformaldehyde, Hydrogen Peroxide, Hydroxylamine, Hydrazine, Cyclopropenylidene, Vinyl Alcohol, Ethylene Oxide, Formic Acid, and Cyanamide are not involved in viable reactions which reduce Na^+ concentrations in interstellar clouds.

7 References

[1] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem Phys.* **1991**, 94, 7221.
[2] Petrie, S. *J. Phys. Chem.* A **2001**, 105, 9931.
[3] Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, 76, 5183.
[4] K.F. Lim, Program COLRATE. QCPE 643: Calculation of gas-kinetic collision rate coefficients. Quantum Chemistry Program Exchange, **14** (1), 3 (**1994**).
[5] Herbst, E. *The Astrophysical Journal.* **1980**, 237, 462.
[6] Schaftenaar, G. and Noordik, J.H. "Molden: a pre- and post-processing program for molecular and electronic structures", J. Comput.-Aided Mol. Design, 14 (**2000**) 123.
[7] Gaussian 98, Revision A.11.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2002**.
[8] CRC Handkbook of Chemistry and Physics 84th Edition, Lide, D. R. [ed], **2003**, CRC Press, Boca Raton, Florida.