Chemical Events in the Atmosphere and their Impact on Environment
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# QUANTUM-MECHANICAL STUDIES ON THE BINDING PROPERTIES OF SMALL ATMOSPHERE MOLECULES

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## SUMMARY.

It will be shown on selected examples that the methods of quantum chemistry can help to obtain useful information on problems related to atmospheric chemistry.

Model examples will be the study of the competitive clustering of ammonia and water on the ammonium ion and the determination of the characteristics of binding of water, carbon dioxide and sulfur dioxide on the nitrite ion, in relation to gas phase experimental measurements.

A brief account of recent applications to space molecules will be given.

## I. INTRODUCTION

Quantum Chemistry can be utilized in atmospheric research in the same way as in other fields involving molecules and their transformations. Atmospheric chemistry is in fact much more favorable than the usual chemist's chemistry for applying quantum chemical methods since it occurs in the gas phase. From that point of view, of course, space chemistry, where temperature and pressure are very low, is even closer to the ideal conditions! Quantum theory in atmospheric research can be useful in various areas: i) pure spectroscopic calculations of frequencies and intensities, helping the identification and understanding of observations, ii) establishment of potentials for use in collision theory, iii) calculations of the characteristics of clusters (either between neutral molecules or between neutral molecules and positive or negative ions), iv) determination of the energetics and pathways of formation of species and of their properties, etc...

I would like to indicate, on some examples, the kind of information which can be obtained in these calculations. We shall consider first, in some details, the domain of clusters, then make a brief excursion into interstellar space, where a similar approach will give us an insight into recent spectroscopic and reactivity applications.

## II. Energetics and Properties of Ionic Clusters

Clustering reactions of neutral species around positive and negative ions play a considerable role in the atmosphere (Castleman Jr., 1983; Ferguson and Arnold, 1981). Thus knowledge of the energetics and properties of ion clusters is a prerequisite for an elaboration of proper theories of such phenomena as nucleation and condensation.

A considerable progress towards the understanding of ion-molecule interactions has been made possible in the last decade due to two simultaneous developments: one concerns the establishment of experimental methods for measuring, in the gas-phase, the characteristics of association in high pressure mass spectroscopy (Kebarle, 1977; Tang *et al.*, 1972), ion-cyclotron resonance spectroscopy (Beauchamp, 1971), flowing-afterglow systems (Ferguson *et al.*, 1969). The second development which occurred simultaneously, is the progress made in the non-empirical techniques of quantum chemistry which rendered possible the calculation to a fair accuracy, of the energies of interaction between ions and ligands. The comparison of the computed energies with the measured enthalpies of binding provides a unique way to test the accuracy of the theoretical calculations; at the same time, the interest of performing such calculations in connection with gas-phase measurements resides in the fact that, aside from binding energies, they furnish, as subproducts, quantities which are not attainable by direct measurements, such as for instance, the equilibrium structure of the adduct (distance, angles), the lability of the binding (how much energy is lost upon displacement from equilibrium), as well as informations on the nature of the interaction, since it is possible to define and evaluate explicitly, inside the binding energy, the separate values of its main components (electrostatic, polarization, repulsion, charge-transfer and dispersion). Thus the conjunction of the two developments mentioned above renders possible a clearer rationalization of the phenomenon of cluster formation.

To illustrate the kind of information obtained let us consider two examples.

The first concerns the clustering of ammonia and water molecules around the ammonium ion, which was one of the first successes of theory in this domain. The extent to which the conclusions drawn at the beginning have remained stable throughout the refinements of the theoretical methodology is a good illustration of what can and what cannot be asked from calculations at different levels of accuracy. It must be said that although the presence of $NH_3$ in the low atmosphere is suspected, due to the biological activity of soils (Fehsenfeld and Ferguson, 1973 and references therein) and the presence of $NH_4^+$ mixed clusters advocated (ibidem), there do not seem to be direct *in situ* measurements to support it. Thus our example has more didactic value than direct bearing on an observed atmospheric chain of events.

Early mass-spectrometer studies (Hogg and Kebarle, 1965; Hogg *et al.*, 1966; Searles and Kebarle, 1968), confirmed later by different groups and techniques (Payzant *et al.*, 1973; Fehsenfeld and Ferguson, 1973; Tang and Castleman, 1975) of the competitive solvation of $NH_4^+$ by water and ammonia vapors had shown that $NH_3$ molecules were taken up preferentially to water, up to an addition of four molecules in the first solvation shell, while water seemed to be preferred over ammonia in the second solvation shell.

The situation was viewed at first as somewhat surprising since, in such interactions, considered to be essentially ion-dipole interactions, the molecule with the larger dipole moment, water ($\mu = 1.85$ debye units) should have been taken up preferentially to ammonia ($\mu = 1.47$).

Considerations on the possible importance of polarizability, larger for ammonia than for water, led to require a very small radius for $NH^{4+}$. Hence it was suggested that the arrangement of the ammonia molecules around the ion might be of type I (inclusion between $N^+H$ directions) instead of II (hydrogen bonding along $N^+H$ bonds), although no definite choice could be made (fig. 1).

Three problems were immediately considered by theoretical calculations: i) the structure of the adduct; in other words, the answer to the question whether there is preference for binding along an NH bond or to the central nitrogen; ii) the reasons for the energetical preference for

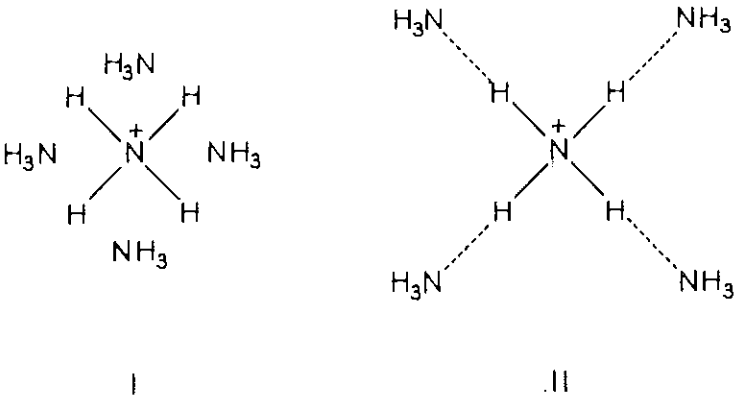
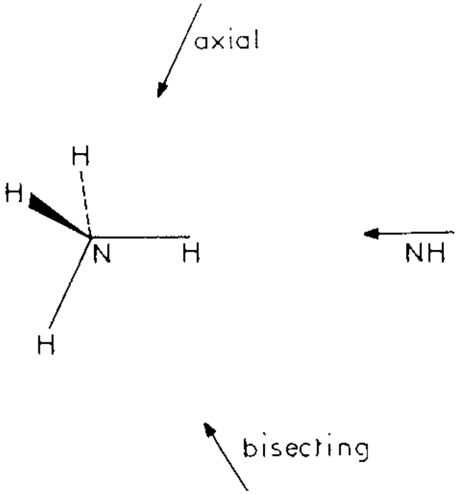


FIG. 1. The two possible structures proposed for the $NH_4^+$ clusters.

$NH_3$ rather than water in the first shell; iii) the reasons for the reversed preference in the second shell. In supermolecule *ab initio* calculations using STO 3G and 4-31G basis sets, (Pullman and Armbruster, 1974) the approach of one molecule (water or ammonia) to $NH_4^+$ was first considered, optimizing the energy with respect to the distance and the relative orientation of the ion and solvent molecules. Three directions of approach were selected: one along the NH bonds, one bisecting two NH bonds in their plane, and one bisecting the angle made by three NH bonds. Rotation of water or ammonia about the direction of approach was allowed in each case so as to obtain the most stable arrangement.

The results summarized in figures 2 and 3 allowed two clear-cut conclusions: a) for both $NH_3$ and $H_2O$ the most stable adduct is, by far, the one which involves fixation along an NH bond, in strong preference to a bisecting position, b) the affinity of $NH_4^+$ for $NH_3$ is clearly larger than its affinity for water.

Further computations on the polyadducts (Pullman and Armbruster, 1975; Pullman, 1976), up to five molecules of $NH_3$ or $H_2O$, gave the results indicated in Table 1 and figure 4 on the evolution of the binding energies upon progressive solvation. The reversal of the ammonia-water preference after $n = 4$ appears very clearly in the results. The parallelism in evolution of the theoretical and experimental data is quite striking, in spite of the numerical overestimation of the values of the binding energies, particularly for small n. This overestimation is a well-documented effect of the STO 3G basis. It was shown later that improvement of the values



Values of $\frac{-\Delta E}{(\text{kcal/mole})}$ and R(Å) (STO 3G)

| Solvent | | NH | Bisecting | Axial | Exp. |
|---|---|---|---|---|---|
| $NH_3$ | $-\Delta E$ | 42.2 | 16.2 | 14.3 | 24.8 |
| | $R_{NN}$ | 2.5 | 2.8 | 2.75 | |
| $H_2O$ | $-\Delta E$ | 37.3 | 16.0 | — | 17.3 |
| | $R_{NO}$ | 2.4 | 2.6 | — | |

FIG. 2. The three directions of approach and their binding energies.

occur, upon enlarging the basis, without altering the rest of the afore-mentioned conclusions. An illustration of the situation is given in Table II. It shows in particular that the preference for the direct NH binding is conserved in all, up to the most refined very recent, calculations. This may be considered as a reflection of the distribution of the positive charge in the ammonium ion among the four hydrogens as exemplified in figure 5.

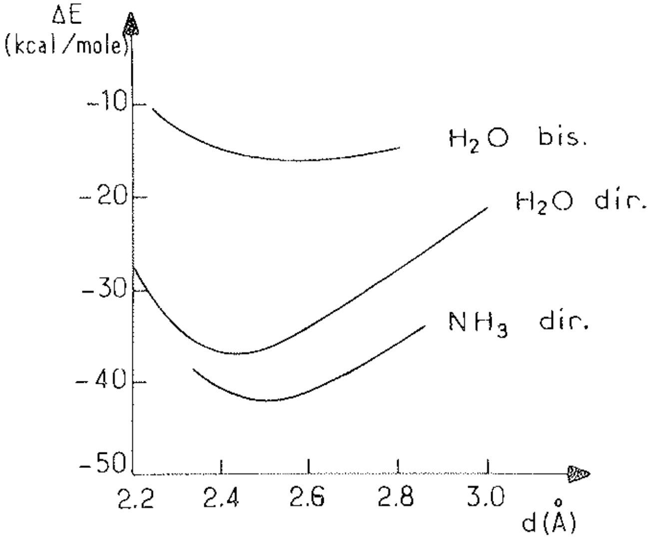


FIG. 3. Evolution of the binding energies of $NH_3$ or $H_2O$ along the approach in different positions as indicated. (dir. = approach to NH; bis. = along bisectrix).

TABLE I - *Stepwise solvation of* $NH_4^+$.

| | n | (a)<br>d | (b)<br>$-\Delta E_{n-1,n}$ | (c)<br>$-\Delta H_{n-1,n}$ |
|---|---|---|---|---|
| Ammoniation | 1 | 2.50 | 42.2 | 24.8 |
| | 2 | 2.60 | 32.0 | 17.5 |
| | 3 | 2.65 | 23.1 | 13.8 |
| | 4 | 2.70 | 17.6 | 12.5 |
| | 5(d) | 2.90 | 10.3 | 7.5 |
| Hydration | 1 | 2.40 | 37.2 | 17.3 |
| | 2 | 2.45 | 28.4 | 14.7 |
| | 3 | 2.55 | 22.1 | 13.4 |
| | 4 | 2.60 | 17.6 | 12.2 |
| | 5(d) | 2.62 | 12.6 | 9.7 |

(a) Computed N ... N or N ... O distance (Å).
(b) Computed (STO 3G), kcal/mole.
(c) Experimental enthalpy, kcal/mole.
(d) With the first four molecules fixed at the equilibrium distance of the tetrasolvate.

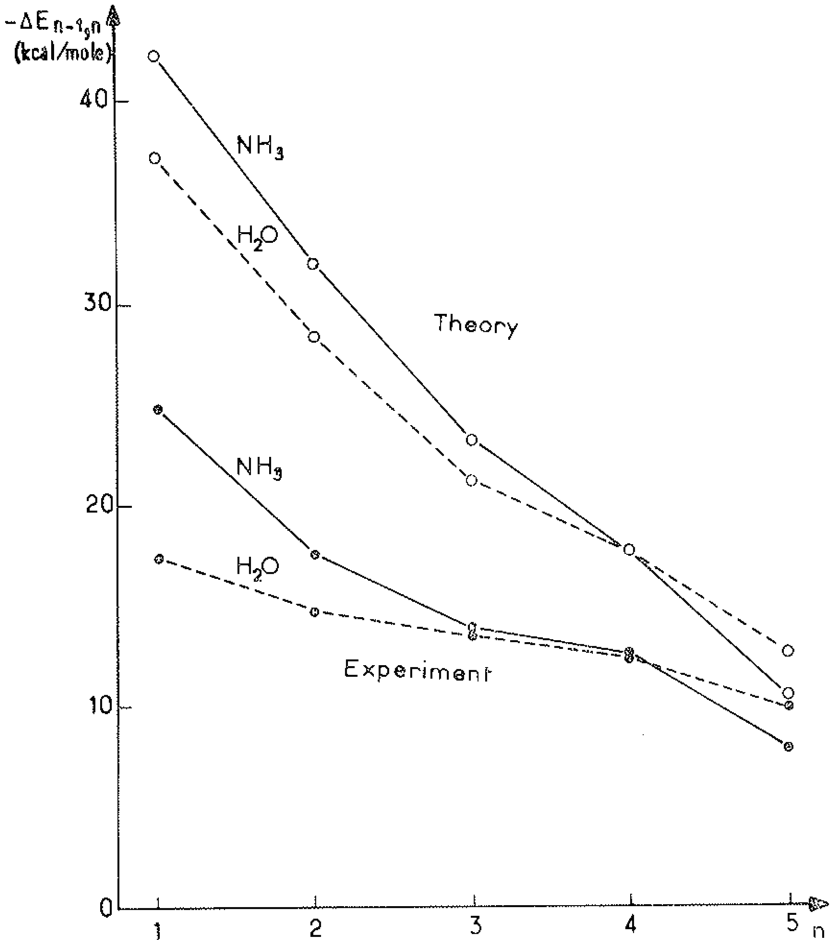


FIG. 4. Evolution of the computed and measured binding energies upon progressive solvation for $NH_3$ and $H_2O$.

by the distribution of the net electron populations. (STO 3G and most accurate calculation of Table II). A still more accurate view of the distribution of the attractive character of the ion towards an incoming nucleophile is given by the distribution of its electrostatic molecular potential (see Scrocco and Tomasi, 1978, for definition) on spheres centered on the nitrogen atom. The values of Table III are seen to be on all spheres in the order: direct > bisecting > axial.

TABLE II - *SCF Binding energies* ($-\Delta E$) *of* $NH_4^+ \ldots H_2O$ *in different basis sets for the positions defined in figure 2 (kcal/mole).*

| | | direct | bisecting | axial |
|---|---|---|---|---|
| 4-31G | (a) | 27.3 | 21.8 | 20.4 |
| PBG | (b) | 22.7 | 16.3 | 14.9 |
| D** | (c) | 20.19 | 17.16 | 16.17 |
| 6-31G** | | 21.6 | — | — |
| DK | (d) | 19.7 | — | — |
| PCC | (e) | 18.51 | 15.41 | 14.56 |

(a) Pullman and Armbruster, 1974; Kollman *et al.*, 1977.
(b) Minimal basis set defined in Pullman *et al.*, 1976.
(c) Dunning polarized (details in Berthod and Pullman, 1980).
(d) Diercksen analog. (details as in (c)).
(e) Pullman *et al.*, 1984.

The underlying features which command the order $NH_3 > H_2O$ in the binding to $NH_4^+$ and the reverse order in the second shell were tentatively rationalized (Payzant *et al.*, 1973) on the basis that the proton affinity of $NH_3$ being larger than that of $H_2O$, its attraction for the positively charged hydrogen of $NH_4^+$ should be larger, an effect which would be superseded in the second shell hy the better H-bonding properties of water. Calculations permit a more precise rationalization: the (exact) computation of the Coulomb component of the binding energy shows that

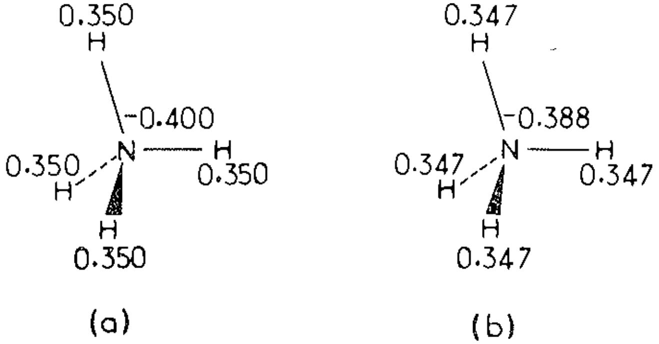


FIG. 5. Net atomic populations in $NH_4^+$ (a) STO 3G, (b) best basis set.

TABLE III - *Molecular electrostatic potential, V(P), of* $NH_4^+$ *on spheres centered on nitrogen (large basis set, see (e) of table II).*

| d (NP) Å | V (P) kcal/mole | | |
|---|---|---|---|
| | direct | bisecting | axial |
| 2.0 | 203.70 | 158.95 | 152.03 |
| 2.5 | 145.41 | 130.13 | 126.23 |
| 3.0 | 116.23 | 109.53 | 107.27 |
| 3.5 | 97.73 | 94.32 | 92.95 |
| 4.0 | 84.64 | 82.73 | 81.85 |
| 4.5 | 74.79 | 73.63 | 73.05 |

it is the major component of the binding energy and that it commands the order $NH_3 > H_2O$ (see Table IV). (Note that this is true in spite of the order $NH_3 < H_2O$ of the dipole moments, because electrostatic interaction cannot be reduced only to the ion-dipole term). On the other hand, in the second shell the new ligands attach themselves to molecules of $NH_3$ or $H_2O$ which, although partially polarized, are more and more similar to "normal" $NH_3$ or $H_2O$ molecules when n increases. In the limit, the respective $\Delta E_{n-1,n}$ must converge towards the hinding energies of the $NH_3$ and $H_2O$ homodimers. These energies (also dominated by the Coulomb energy) as shown in table IV, are in favor of water binding, hence the reversal in tendency. In the homodimers the hydrogen to be bound is

TABLE IV - *The role of Coulomb energy in* $NH_4^+$ *binding and in the homodimers (STO 3G) (kcal/mole).*

| | $-\Delta E$ | $-\Delta E_C$ |
|---|---|---|
| $NH_4^+$ - binding | | |
| $NH_4^+ \ldots NH_3$ | 42.3 | 46.4 |
| $NH_4^+ \ldots H_2O$ | 37.2 | 38.5 |
| Homodimer | | |
| $NH_3$ - $NH_3$ | 3.7 | 4.8 |
| $H_2O$ - $H_2O$ | 5.6 | 6.8 |

appreciably less positive in $NH_3$ (0.160e), than in $H_2O$ (0.183e) so that the fundamentally larger attractive character of $NH_3$ exerts itself on a smaller charge whereas the smaller attractive character of $H_2O$ acts on a larger positive charge: the two effects playing in reverse order, only explicit computations can give a decision. (In fact for $n = 5$, binding occurs to a hydrogen of charge 0.200 in the tetraammoniate and 0.233 in the tetrahydrate, and these charges are much closer to those of the neutral monomers than to the charge of the hydrogen in $NH_4^+$ (figure 5a).

Aside from $NH_4^+$ and apart from the pioneer work on the $H_3O^+$ hydrates (Newton and Ehrenson, 1971), few non-metal positive ions have been studied as extensively by theoretical computations. Very recently, calculations have been done on the proton solvation by methanol and dimethylether (Hirao *et al.*, 1982), and $N_2$, CO and $O_2$ (Yamabe, 1981). In our laboratory, a study of the hydrates of $NO^+$ in view of understanding the mechanism of production of $NO_2H$ is in progress (Pullman and Ranganathan, 1984).

As concerns clustering around negative ions, nearly no theoretical work has been done until very recently on the molecular ions of atmospherical interest other than the water clusters of the spherical halogens. The recent accumulation of gas-phase experimental data on the clustering of neutral molecules on small negative ions (Castleman *et al.*, 1982; Keese *et al.*, 1980) renews the interest in this area by the intriguing regularities (and irregularities) observed. Having studied earlier in some details the binding properties of the phosphate and carboxylate ions, which are of biological interest, (Berthod and Pullman, 1981 and references therein) but for which there are no gas-phase data, we decided to undertake theoretical work on the set of newly measured clusters.

As a first step in this area we have considered the clustering of $H_2O$, $CO_2$ and $SO_2$ to the nitrite ion $NO_2^-$. The experimental data (Keese *et al.*, 1980) show striking differences between the three ligands, their enthalpies of attachment on $NO_2^-$ being $-15.2$, $-9.3$ and $-25.9$ kcal/mole respectively for the first clustering molecule. The rationalization of these results on the simple basis of ion-dipole interaction is obviously not possible. Although ion-ligand interactions are likely to be dominated by electrostatic forces, it was interesting to try and evaluate in the case of these three quite different molecules the relative weights of the components of the binding energies which are perhaps the source of their different behavior. On the other hand, the building up of polymolecular clusters around polyatomic ions strongly depends not only on the structural properties of the ion itself and on the distribution in space of its attractive character but also on the most advantageous location of the first molecule in the cluster, which itself depends on the properties of the ligand. Owing to the differences between water, carbon dioxide and sulfur dioxide, the question of the location of the first molecule is not purely academic.

For this exploratory study we used a minimal but good quality basis set, which we found could reproduce, to a fair accuracy, the results of much more extended basis for anion binding (Berthod and Pullman, 1981). Technical details for the present problem can be found in the original paper (Pullman and Berthod, 1981).

Concerning the structure of the anion itself, the image given by the computed electron populations indicates a slightly positive nitrogen atom (global charge 6.983 $e^-$), the negative charge being essentially shared by the two oxygens (8.508 $e^-$ each). This excess negative charge is essentially of $\pi$ character (1.512 $e^-$ on each oxygen, 0.976 $e^-$ on the nitrogen). A somewhat more informative view of the structural properties of $NO_2^-$ is given by the distribution of its molecular electrostatic potential (fig. 6). It is seen that the negative potential entirely surrounds the ion. Quite striking is the fact that a very deep minimum faces the nitrogen atom ($-200$ kcal/mole), very close in value to the two minima associated with each oxygen atom. This shows once more that reasoning purely on electronic charges can be misleading.

The overall distribution of the negative potential indicates that the whole molecular periphery will be able to present a favorable attractive interaction with an electrophile, with perhaps a small advantage in favor of the oxygen regions. In order to gain more information on the role of the pure electrostatic energy in the binding, the search for the binding characteristics was done in two steps: first using a procedure developed in our laboratory (Pullman and Perahia, 1978, and references therein) where a good approximation of only the electrostatic part of the interaction is calculated, then by complete supermolecule calculations to find the energy and the most stable positions. The results of the calculations led to the following major conclusions:

1) The binding energies computed for single attachment in the most favorable positions for $H_2O$, $CO_2$ and $SO_2$ (Table V) are in very good agreement with the measured enthalpy values. The agreement is sufficiently good to lend credence to the conclusions concerning the binding positions. For water, a calculation with a better basis set (Banerjee *et al.*, 1980) confirms entirely our data with a somewhat less good binding

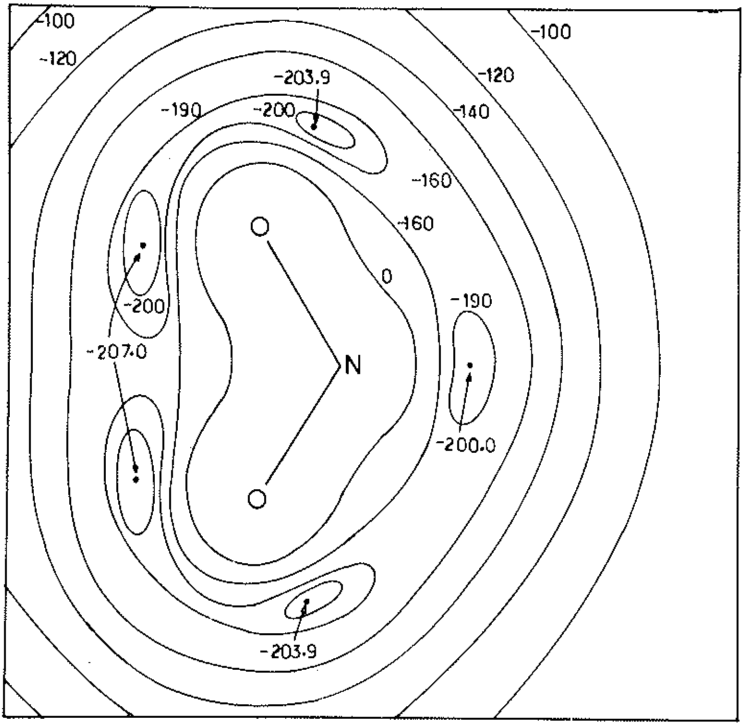


FIG. 6. The molecular electrostatic potential of $NO_2^-$ in the plane of the ion (values in kcal/mole).

TABLE V - *Best location and binding energy (kcal/mole) of* $H_2O$, $CO_2$ *and* $SO_2$ *on* $NO_2^-$.

| | d (Å) | $-\Delta E$ | $-\Delta H$ (d) |
|---|---|---|---|
| $H_2O$ | 2.9 (a) | 15.4 | 15.2 ± 0.1 |
| $CO_2$ | 2.7 (b) | 8.2 | 9.3 ± 0.1 |
| $SO_2$ | 2.2 (c) | 26.1 | 25.9 ± 0.2 |

(a) O . . . O distance; water bridging the two oxygens of the anion; coplanar arrangement.

(b) O . . . C distance V; C on the bisectrix of ONO; $CO_2$ perpendicular to the ONO plane.

(c) S . . . O distance, $SO_2$ perpendicular to ONO plane, NOS angle = 110° bisectrix of $SO_2$ at 50° from O . . . S direction.

(d) Keese *et al.*, 1980.

energy. Our least satisfactory agreement occurs for $CO_2$. It is possible that this is due to the relatively poor representation of the polarisability in our small basis set. This point is being explored by more refined calculations.

2) The pure electrostatic exploration indicates in all cases, in accord with the complete calculations, the most favorable orientation of the ligand to be in-plane for water, perpendicular to the plane for $CO_2$ and for $SO_2$. Furthermore it points out that the most favorable positions at the periphery of $NO_2^-$ should he on the internal bisectrix (position $B_1$) for water and $CO_2$, tbe external bisectrix (position $B_2$) being much less favored. It also indicates that a rather wide region of possible binding exists in the lateral region external to the ONO angle and in its symmetrical counterpart (position E). When the complete interaction energies are calculated, they show that, in agreement with these indications, the most stable positions of water are in the order $B_1 > E > B_2$ (figure 7) with a large lability in the neighbourhood of the best E position. Very similar results are obtained for $CO_2$ where the regions of most favorable binding are also those indicated hy the pure electrostatic data (see Pullman and Berthod, 1981, for details).

The case of $SO_2$ offers a more complex situation. As for tbe two other ligands the electrostatic results point to three areas of favorable interaction: the inner bisectrix region, the external bisectrix region and

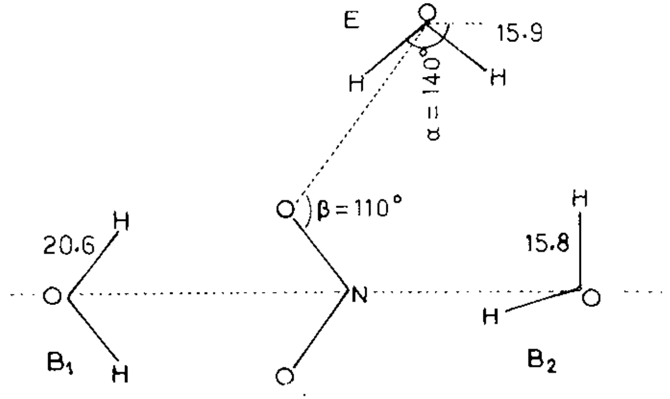


FIG. 7. Best positions and energies in the pure electrostatic search for the arrangement of water around $NO_2^-$.

an intermediate domain in the exterior of the ONO angle (fig. 8). The differences in the energy values are not very marked, however, an indication that other components of the binding energies can reverse the final order of the positions. Indeed the complete computation (Table V) indicates that the preferred position is external. Moreover it is followed by another angular position I internal to the ONO angle (see figure 9), nearly symmetrical from E with respect to the NO bond, then by the two bisecting positions, but with $B_2$ this time more favorable than $B_1$.

A further analysis of the data indicates that the element responsible for the difference in the order of the electrostatic and total energies is the charge transfer component of the binding energy: the amount of electron population transferred to $SO_2$ by the ion was computed as 0.331, 0.273, 0.211 and 0.169 $e^-$ for positions E, I, $B_2$ and $B_1$ respectively. (In the best $CO_2$ adduct it was only 0.048, and in the best water complex 0.008). This confirms the partial charge transfer character of the $SO_2$ adduct suspected by Keese *et al.* (1980) on the basis of the strong electron affinity of $SO_2$. Interestingly our calculations have shown that the lowest empty molecular orbital of $SO_2$, which is indeed very low, is a $\pi$ orbital, thus perpendicular to the molecule. It is notable that the orientations favored by the electrostatic energy, are thus also those in which this empty orbital is oriented at best to receive the transfer from both O and N of $NO_2^-$. The preference of $B_2$ over $B_1$ is also clearly related to the charge transfer effect which is favored on the nitrogen side.

The consequences of the partial charge transfer character in the $SO_2$ adduct may affect in an interesting fashion the binding of further molecules in the cluster. We are pursuing the explorations of these problems, as well as that of the $CO_2$ polarization and intend to utilize the experience acquired in this study for investigating clusters around more abundant atmospheric ions, particularly $NO_3^-$.

## III. An Excursion in Space

Although the object of the present Study Group is not the study of molecules in the interstellar space, I would like to mention briefly some contributions of quantum chemistry in this domain where neither the methodologies nor the molecular problems are fundamentally different from those occurring in atmospheric research.

There are three essential areas where quantum chemistry can provide

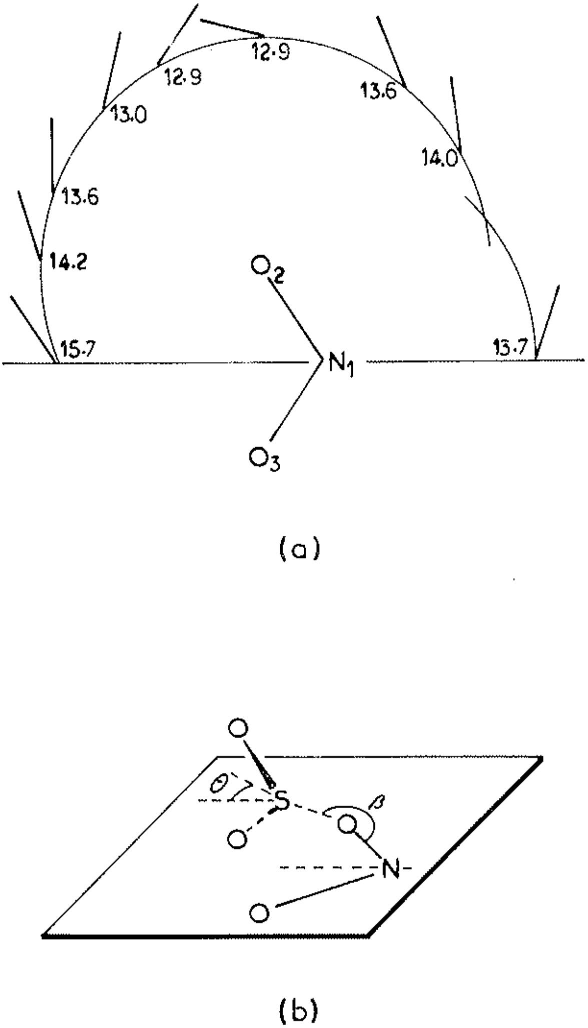


FIG. 8. a) The preferred orientation of the plane of $SO_2$ in the mutual perpendicular arrangement when the S atom moves around the periphery of the nitrite ion (values of the electrostatic interaction as indicated, in kcal/mole; $O_2 \ldots S$ or $N \ldots S = 2.6$ Å). b) Angles defining the position of $SO_2$ with its sulfur atom in the plane of the nitrite ion. $\Theta$ is the angle of the bisectrix of $SO_2$ with $N \ldots S$ for bisecting positions, with the direction of the bisectrix of ONO for the more general case. $\beta$ is the NOS angle.

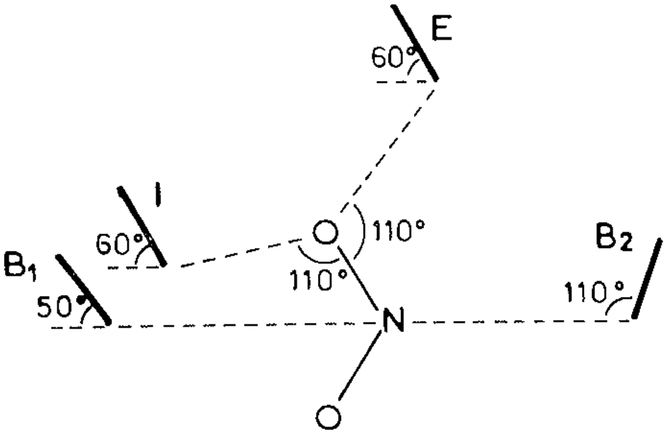


FIG. 9. Location of the minima of the energies of interaction (SO2 perpendicular to the plane with its bisectrix oriented as indicated).

useful informations in Astrochemistry: i) computation of molecular geometries and dipole moments, from which can be deduced the frequencies and intensities of rotation spectra, ii) calculation of energy balances for formation and destruction of species, very often ion-molecule reactions, iii) obtention of potential energy curves to be used in the theory of collisions between molecules, electrons and photons. Thus, when a rotation line is detected its attribution to a given species can be helped by a theoretical calculation in the absence of a laboratory spectrum. A well-known example of such a situation in the recent past was the attribution of the so-called X-ogen line to $HCO^+$. A more recent example concerns the identification of $HCS^+$ by its computed rotation line. On the other hand the value of the dipole moment of a species (which determines the intensity of the lines) indicates whether its detection by radiotelescopes is likely. Finally the energy balances computed will indicate the probability of formation of a given species, taking into consideration the fact that in the interstellar conditions of low densities and low temperatures only exothermic reactions and transformations with low activation energies can occur.

Let us mention two very recent studies along these lines. After the identification of $HCS^+$ as responsible of a rotation line observed at 85.387 GHz (Chekir *et al.*, 1983) and its near-simultaneous confirmation by a laboratory spectrum, the possibility of existence and detection of the sister species $HSC^+$ was considered (Berthier *et al.*, 1983). Table VI indicates the dipole moments computed for the known and unknown species as well as the energy balance for their formation in different possible reactions. Both the energetics of the reactions and the computed dipole moments of the two species led the authors to conclude a small probability of detecting $HSC^+$.

The second study concerns the silicium analogs of the $HCO^+/HOC^+$ and $HCS^+/HSC^+$ pairs (Berthier *et al.*, 1984). The essential results sum- $HOSi^+$ would appear to be, by far, the most likely to exist (large exothermicity of production) but its dipole moment is so weak as to make its detection impossible, whereas its isomer, which could be detectable, appears difficult to form. The corresponding sulfur compounds present a much smaller difference in stability and may probably form. Furthermore they have sufficiently large dipole moments to he good candidates for detection. For the most stable one, the predicted rotation spectrum has been calculated.

## IV. CONCLUSION

In this brief summary, I have attempted to give an idea of some of the areas in which quantum chemical calculations can be helpful to the experimentalist in atmospheric or space chemistry. Although the prediction of very accurate binding energies, reaction balances or rotation lines require the use of the most elaborate versions of theory and although they generally cannot be considered as substitutes for an experimental

TABLE VI - *Computed dipole moments (debye units) and energy balances for different forming reactions for* $HCS^+$ *and* $HSC^+$.

| | $HCS^+$ | $HSC^+$ |
|---|---|---|
| $\mu$ (D) | 2.2 | < 1.3 |
| $CS^+ + H_2$ | − 41 kcal/mole | + 31 kcal/mole |
| $C^+ + H_2S$ | − 136 » | − 64 » |
| $CS + H_3^+$ | − 90 » | − 18 » |
| $CS + H^+$ | − 196 » | − 124 » |
| $CS^+ + H$ | − 146 » | − 74 » |

TABLE VII - *Computed energy differences, dipole moments and energy balances in formation reactions for the* Si *analogs of* $HCO^+$ *and* $HCS^+$.

| | HOSi | HSiO | HSSi (b) | HSiS |
|---|---|---|---|---|
| Energy (kcal/mole) | – 65 | 0 | – 16 | 0 |
| $\mu$ (D) | 0.02 | 6.48 | 2.82 | 4.83 |
| (a) Balance (kcal/mole) | – 46/– 198 | + 19/– 133 | – 3/– 106 | + 13/– 90 |

(a) in reactions analogous to those of table VI.
(b) bent.

measurement, there are clearly areas where careful systematic studies may lead to predictions or rationalizations which can be used as a guide to further experimentation and better understanding. It is my hope that our encounter at this meeting will help establish contacts for a still more useful collaboration.

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## DISCUSSION

CHAMEIDES

How many ligands make up the first shells on $NO_2$?

PULLMAN

It depends on the ligands; 3 or 4. $CO_2$ has not been studied beyond 1 molecule, but for $SO_2$ it is of the order of 3 to 4 — a small number.

CHAMEIDES

Is the definition of the second shell that the ligand of the second shell attaches to the ligand of the first shell? Is that by definition?

PULLMAN

Yes, that is my definition.

CHAMEIDES

I have another simple question. The difference between the bisecting binding and the direct binding of $NH^+_4$ — this one that you showed, is that direct? It looks like it is bisecting to me. Could you explain the difference?

PULLMAN

In figure 2 is the correct drawing of $NH^+_4$ and the definitions: direct approach to NH, bisecting in the plane (hisecting the angle of two NH bonds), axial in the prolongation of the NH, on the axis of the molecule in between the three other hydrogens on the other side.

ARNOLD

First of all, a brief comment on the first question or discussion about the definition of the first shell and the ammonia clusters. There is an additional piece of information from energy measurements by Kebarle and colleagues. They studied the mixed clusters containing both ammonia and water molecules and they found that the mixed clusters contain only up to 4 ammonia molecules, and the rest of the ligands would be water molecules. Then another brief comment: you mentioned that the ammonium ion clusters may not be of importance; at least in the atmosphere they have not been measured. It seems from recent studies that they can be quite important, and it can also be found from the laboratory measurements at our institute that ammonia reacts with the other mixed clusters which have been observed in the lower parts of the atmosphere, namely those containing water and another molecule having large proton affinity, not as large as ammonium. It appears that ammonia also reacts with these cluster ions forming even more complex clusters containing several molecular species as ligands. And then a brief question: you mentioned that in future work you will focus also on calculations of a bit larger clusters — you mentioned second shell or more ligand molecules. How urgent would these calculations be? How are the prospects for those calculations? How accurate would these calculations be? We have seen from your discussion that you can calculate rather accurately the bond energy for smaller systems containing an ion and one ligand molecules, and we have seen that the calculations for the more complex systems were capable of giving an order of magnitude, a sequence and things like that but not necessarily very good absolute numbers for these $\Delta H$ values.

PULLMAN

Yes, that is a very good remark, because you have to be extremely careful. As I said, for the ammonia problem it was very lucky that the very small basis set used at the beginning was able to go so far and that the results were confirmed upon improvement of the basis later without change in a qualitative sense. Generally this small, (very small) basis sets. STO 3G is a bit dangerous in these areas, and I would not nowadays (this was ten years ago) use it to start the calculations. However, the way to deal with this problem is the following: there are now a number of calculations of very accurate energies, particularly on the metal cations and on a few molecular ions. On the other hand there exist possible tests of these energies by measurements of enthalpies of binding in the gas phase. Thus, once you know that a very good theoretical calculation reproduces the experimental energy results you can try to taylor a smaller basis to reproduce all the characteristics (not only the energies) given by the best existing calculation. This is what we have done for the metal cations, lithium, sodium, and potassium, for instance. And we have found a basis set which is appropriate to reproduce the binding energy and the rest to a fair accuracy. It is not quite as good as the final values you have seen, but for most purposes it is quite good. Of course there is always a possibility of an artefact which has not been detected. The best thing, if you can, is to take the best available method, of course, but it is not always possible. I do not think that for the second molecule of $SO_2$ going on $NO^{-}_2$, it would be possible to go to the most accurate calculations. Thus one must try otherwise, and if possible perhaps do it by calculations of two different accuracies. But the philosophy is always: obtain as much as possible information with a very good calculation, try to find a basis set which reproduces it and then use this basis to go over to more complicated systems involving the same ligands.

CANUTO

Would you be kind enough to tell me how many free parameters do you have when you begin your computations? because I was struck by your statement at the end, something about the rotational energy not being as reliable as something else.

PULLMAN

You generally want a rotational energy to the second decimal place after the point. This is too much to ask at present except perhaps for very small systems.

CANUTO

The only experience I have in nuclear physics when you compute the rotational energy of the one for which you have an analogy is ask the easiest one to compute. Here it seems to be the other way around. But how about the free parameters? How many free parameters would you say you have at the beginning?

PULLMAN

In a computation of the kind of clustering reactions, between molecules you need the positions of the atoms for each ligand, that is the distances and the angles (and even that you can nowadays optimize if you wish). That is one input; the other input is the basis set, namely the linear combination of atomic orbitals in terms of which you decide to develop your molecular orbitals. Now this is not an empirical parameter, it is a choice: you decide that you are going to express your molecular orbitals as a linear combination of a certain set of atomic orbitals. If you choose a small number (small basis set) you have a poor result, energy speaking; if you choose a very large basis set you have a much better energy. That's all — and you compute the wave function of all the electrons in the field of all the nuclei in each configuration of the system. There is no empirical parameter properly speaking.

CANUTO

Your variable D that you gave as a number — that was a variation parameter, was it not? When you showed the energy versus D and it was shallow...

PULLMAN

Yes. When you search for the equilibrium position of two ligands, you start with, say, your water molecule somewhere at a certain distance of the ion, compute the wave function of the whole system and its energy, then vary the distance, find the energy, etc. Doing so along an axis yields a minimum in the curve at some place. Generally you also rotate your molecule in all possible directions looking again for the minimum. Overall you make a very detailed span of the so-called "hypersurface of interaction". It has to be done in a detailed way, otherwise you may miss unexpected minima. For example the external position for $SO_2$ and its angular position with respect to the $NO_2$ molecule would be difficult to guess a priori. I may add one thing on this occasion, which concerns the slide I passed, which concerns the problem $H_2O$ clustering on $NO^+$. It was posed to us by E.E. Ferguson who wanted to know the structure of tetrahydrate of $NO^+$ in order to understand the production of nitric acid. To start this problem we searched first the structure of the monohydrate with a very large basis set; the detailed span of the surface has shown that the position of a first water molecule is neither direct to nitrogen nor direct to the oxygen, but is an external position, on the side of the ion, difficult to guess a priori.

ROWLAND

A comment about two calculations that had to do with the stratospheric chemistry. I would like to make a comment and ask for your comments on that. The first one had to do with where in the first place I think that quantum mechanics was brought in as an attempt to solve a problem that was very pressing at the time which was the question of the proto-absorption coefficients for the molecule HOCl, and the calculation that was done on HOCl said that there should be very little absorption out beyond 300 nanometers — this was given some publicity in Chemical Engineering News as being a solution to a problem by quantum mechanics. However, the experimental measurements did not reproduce the theory and showed that there was substantial absorption, sufficiently that HOCl is photochemically quite active out beyond 300 nanometers. That is one comparison.

The other is a calculation that was done at Irving by the research group of Warren Hehre, with Michel le Fanson working on it. She was interested and did calculations on the possible isomers of chlorine nitrate, a question that has been of considerable interest in terms of the chemistry as to how the free radicals ClO and $NO_2$ might combine. The conclusions that she came to were two. One of them is that on an energetic basis the only isomer of chlorine nitrate that is feasible energetically is chlorine nitrate itself. The molecule ClO ONO is about one electron-volt higher. It does show a minimum in the potential but it is probably not going to be able to be formed under stratospheric conditions. She then tried to calculate the infrared spectrum of this molecule ClO ONO in order to know how one might look for it, that is just to confirm it experimentally. But she gave up on that because she found that with the heavier atom chlorine the calculation for chlorine nitrate itself did not reproduce satisfactorily the known infrared spectra there. So since it did not reproduce a known molecule then it was not going to be useful for a search for an unknown molecule.

Those are the two cases that I know of in the stratospheric chemistry where there have been attempts to apply quantum mechanics directly to the problems as they were being considered at the time. The question is: when do you think we will start being able to get quantum mechanical calculations that are competitive with experiments for solving some of these problems?

PULLMAN

I agree completely with you, and I mentioned it, I think, at the end of my talk. In the two problems you quoted, one faces the most difficult things to do, particularly when there is a "heavy" atom. When can we do this kind of computations? For smaller molecules it is more hopeful, and I mentioned briefly examples but as I said, calculations there give only an indication; for instance if it is worth looking for a laboratory spectrum. Very often, in space chemistry for instance there is an observation of a certain rotation line. One suspects two possible candidates to be responsible for it. There is no laboratory spectrum for either one. Which one are you going to try and handle first?

If a reasonably accurate calculation is possible I would suggest to undertake it, and this is what has been done for a few cases. But for a molecule like those you mentioned, accurate enough calculations are not yet feasible. When is it going to be possible? Well progress goes very fast. If you would tell me, when we did the $NH^+_4$ calculations ten years ago, that I would be able to do it now to the bitter end, that is, to be able to reproduce a numerical value of the binding energy, I would be dubious. Ten years after, it is nearly standard calculation, although still very expensive. I told you that the rotation lines are one very difficult thing to compute precisely. So are also exact balances of energy in reactions or in comparing isomers. According to the refinement of the calculation you can make minima appear which had not been seen before especially when radicals are involved. Clustering reactions are easier to deal with. I have tried at least to tell you what can be done and what cannot (yet).

ARNOLD

A very brief comment: there is a famous example of the application of quantum chemistry, the one which you have briefly mentioned, namely the detection or the identification of the so-called X-ogen line in interstellar space, which was identified as $HCO^+$ and this opened an entirely new avenue to interstellar chemistry and molecule formation, namely, it stimulated the discussion about the possibility of ion-molecule reactions being responsible for the formation of many of the molecular states.

PULLMAN

Yes, It is the same with $HCS^+$. In fact the calculation has been done and the laboratory measurements on the spectra have been done in parallel, and it was a convergent effort; and I think this is the way quantum chemistry should be used, not pick a calculation and say: it doesn't fit; theory is no good. First, theorists should work in close connection with experimentalists. And experimentalists, in particular in atmosphere chemistry should ask the questions which they would like to have answered from the quantum chemists. I think this might help sometimes.

ROWLAND

I would comment also that the calculations of the bond distances for chlorine nitrate are very close to the experimental values. It works very well for that.