STUDY OF POTENTIAL CURVES BY UHF TYPE METHODS. INVERSION AND DISSOCIATION OF NH_3 MOLECULE

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Geometry and energy parameters of individual dissociation intermediate steps of the NH_3 molecule, geometry of the saddle point, and the inversion barrier of NH_3 have been calculated by the UMP2 method in the minimum basis set augmented with the bond functions. A good agreement has been reached with experimental data and with results of more exact methods except for the dissociation energies of the NH_3 and NH_2 molecules. New values of heats of formation are suggested on the basis of these results: $\Delta H^0_{f0} = 197$ and 362 kJ/mol for the NH_2 and NH molecules, respectively.

The NH_3 molecule and its chemical reactions belong to chemical systems frequently studied by quantum-chemical methods. This attention is due mainly to the need for exact data about electronic structure of NH_3 and the therefrom following spectroscopical characteristics which are very important for cosmochemistry, chemistry of upper layers of the atmosphere, as well as in the field of construction and application of the lasers. On the other hand, numerous calculations of various properties of this molecule have ranged it among such molecules whose known experimental parameters are used as touchstones for verification of quality of quantum-chemical methods. Similarly, the present communication representing a continuation of the previous series[1-6] has the aim to continue the testing of the UHF type methods in connection with the standard basis set.

The UMP2 method[7] used in the present work combines the advantages of correct description of the dissociation limits by means of the UHF reference function with the simplicity of inclusion of the correlation effects on the basis of the Moller–Plesset perturbation theory[8] in the second order approximation. The basis set is described in detail in ref.[2], and it represents the minimum basis set extended by a group of six-bond functions of the ($3s$ $1p$) type which are located in the middle of each chemical bond. This methodical approach describes surprisingly well the geometry and energy parameters of splitting or formation of chemical bond between H atom and other light atoms (potential curves of diatomic hydrides[2], characteristical points of the hypersurfaces of $H + H_2 \rightarrow H_2 + H$, $H_2O \rightarrow OH + H \rightarrow O + 2\,H$ reactions[5], dissociation and excitation energies of the B^+, BH^+ systems[9]). This fact is probably explained by the idea that an incomplete description of electronic correlation effects is compensated by means of the bond functions which tend to prefer – to a certain extent – the regions with high electron density. Probably in this way, sufficient compensation is obtained for a part of the so called extra molecular correlation energy which cannot be involved in the UMP2 method. This compensation effect, however, does not suffice for descritpion of dissociation or formation of the bonds between the second-row elements[3,4] and especially in the cases of multiple chemical bonds, where it is necessary to adopt more efficient methods of description of electronic correlation effects.

On the basis of these considerations, a good agreement with experiment can be expected in the case of dissociation and inversion of the NH_3 molecule. The first part of this paper confirms it in the geometry description of the NH_3, NH_2, NH molecules and of the inversion saddle point. The second part of this paper points at the good agreement in the case of the dissociation energies of the individual dissociation steps and the activation barrier of the NH_3 inversion. Discrepancies in two cases lead to a suggestion of modified values for heats of formation of the NH_2 and NH molecules.

Geometry Parameters

Optimization of the geometry parameters in the NH_3, NH_2, NH molecules as well as in the planar configuration of NH_3, which corresponds to the inversion saddle point, gave the equilibrium distances and angles presented in Table I. The obtained data agree well with experiment. The UMP2 method in the basis used overestimates slightly – in all the cases – the equilibrium distances and angles. Also interesting is the comparison with the available *ab initio* results obtained with application of substantially greater bases and more exact ways of inclusion of the correlation

TABLE I

Calculated and experimental values of equilibrium N–H distances (R_e) and equilibrium H–N–H angles (Θ_e)

Molecule	$R_e^{calc.}/10^{-10}$ m	$R_e^{exp.}/10^{-10}$ m	$\Theta_e^{calc.}/^0$	$\Theta_e^{exp.}/^0$
NH_3	1·03	1·013[a]	107·5	107·03[a]
NH_3 planar	1·01	0·999[d]	120·0	120·0
NH_2	1·05	1·024[b]	103·8	103·4[b]
NH	1·06	1·0362[c]	—	—

[a] Ref.[10], [b] Ref.[11], [c] Ref.[12], [d] Ref.[21].

effects. So, *e.g.*, Rodwell and Radom[13] give (the ($8s\,5p\,2d/5s\,2p$) basis and MP3 method) for the NH_3 molecule the equilibrium distance $1{\cdot}007 \,.\, 10^{-10}$ m and the angle 106·9°. The same authors obtained for the planar geometry of the saddle point of inversion of NH_3 the equilibrium distance $0{\cdot}991 \,.\, 10^{-10}$ m, which – along with the experimental data of Table I – indicates that the equilibrium distances are overestimated in our approach by about $0{\cdot}02 \,.\, 10^{-10}$ m. The equilibrium geometry of the NH_2 molecule was estimated[14] in the ($5s\,3p\,1d/3s\,2p$) basis by the method of multiconfigurational interaction complemented by first order CI calculations. In this way, the values $1{\cdot}051 \,.\, 10^{-10}$ m and 101·14° were obtained. Similarly[7], the values $1{\cdot}026 \,.\, 10^{-10}$ m and 101·7° were determined.in the ($8s\,4p\,1d/4s\,1p$) basis in the UMP2 approach. Comparison with these more exact approaches indicates that our method gives relatively reliable geometry parameters of the systems studied.

Energy Parameters

Estimation of height of the inversion barrier found on the double-well hypersurface of the NH_3 molecule belongs to the problems frequently studied by quantum-chemical methods[13-16]. According to the last calculations[13] in the ($8s\,5p\,2d/5s\,2p$) basis, the magnitude of the barrier is affected but slightly by the electron correlation effects. The value 21·8 kJ/mol obtained at the SCF level is increased to 22·6 and 23·4 kJ/mol in the MP2 and MP3 approximations, respectively. With our basis we obtained the values 17·5 and 21·5 kJ/mol at the SCF and MP2 levels, respectively. Comparison with the above data shows that the difference in the barriers at the SCF level is substantially lowered at the MP2 level, which means that the perturbation way of inclusion of the correlation effects can compensate – to a certain extent – the imperfections of the basis used in this case.

The NH_3 molecule offers an interesting possibility of comparison of the calculated inversion barrier with the barrier determined by theoretical analysis of vibrational-rotational spectra of this molecule[17-21]. However, it must be realized[22] that the value thus obtained corresponds to the NH_3 inversion with constant internuclear N—H distances. So far the most exact approach of anharmonic non-rigid invertor[21,22] gives the barrier magnitude equal to 21·9 kJ/mol which can be compared with the MP2 barrier (in our basis) equal to 24·7 kJ/mol (obtained with constant $r_{N-H} = 1{\cdot}03 \,.\, 10^{-10}$ m).

On the contrary, the quantum-chemical determination of the dissociation energies type D_e for the molecules

$$NH_3 \rightarrow NH_2 + H \tag{A}$$

$$NH_2 \rightarrow NH + H \tag{B}$$

$$NH \rightarrow N + H \tag{C}$$

is rarely submitted to studies[23,24] (partially[7]). For the atomization energy of

$$NH_3 \rightarrow N + 3\,H \qquad (D)$$

at 0 K the value of 1 158·6 kJ/mol was obtained from the heats of formation $\Delta H^0_{f_0}$ taken from the JANAF tables[25], which gives 1 249·2 kJ/mol after the zero point energy correction of NH_3 according to ref.[21]. The UMP2 method in our basis gave the value of 1 247·5 kJ/mol. This surprisingly good agreement with experiment justifies a hope of good agreement in the dissociation intermediate steps $(A)-(C)$. The D_e values are listed in Table II. The experimental dissociation energies were determined from the D^0_0 value[29] of NH_3 in the case (A), from the heats of formation $\Delta H^0_{f_0}$ of NH_2 (ref.[28]) and NH (ref.[25]) in the case (B), and from the D^0_0 value[12] in the case (C). The value of the zero point correction is 90·6 kJ/mol for NH_3 (ref.[21]), for NH_2 and NH it was determined 47·2 and 19·4 kJ/mol, respectively, (the vibration frequencies from refs[12,27]). An acceptable agreement with experiment is obtained only for the dissociation of the NH molecule. Another discrepancy consists in the fact that the sum of the experimental values $\leq$1 237·1 kJ/mol differs markedly from the experimental atomization energy 1 249·2 kJ/mol. As the experimental heats of formation of NH_2 and NH are given with the accuracy of $\pm$10 kJ/mol, it can be expected that these are the very parameters which are the main source of inconsistency of the results. The theoretically determined value of $\Delta H^0_{f_0}$ for NH can be obtained by a reverse procedure from D_e^{calc} of the reaction (C), and for NH_2 from the D_e^{calc} values of the reactions (A) and (B). This procedure gives the value of 361·8 kJ/mol for the NH molecule (experimental value according to the JANAF tables[25] is 339·1 kJ/mol, according to the supplement[30] it is 377·4 kJ/mol, and the last experimental work[31] gives the value of 367·6 kJ/mol). From the reactions (A) and (B) it was obtained $\Delta H_0^{f_0}(NH_2) = 196{\cdot}0$ and 197·5 kJ/mol, respectively, which can be compared with the experimental date[23] 187·1 kJ/mol.

TABLE II

The dissociation energies[a] (D_e) for the dissociation reactions (A), (B), (C) in kJ/mol

Molecule	$D_e^{calc.}$	$D_e^{exp.}$
NH_3	494·5	487·2
NH_2	408·1	395·7
NH	344·9	$\leq$354·2

[a] The experimental data taken from refs[12,21,25-29].

CONCLUSIONS

The geometry parameters of the NH_3, NH_2, NH molecules and of the saddle point of the inversion of NH_3 agree well with experimental data. The same is also true of the inversion barrier of NH_3, atomization energy of NH_3, and the D_e value for NH. As the dissociation energies of the NH_3 and NH_2 molecules showed large discrepancies, the heats of formation $\Delta H^0_{f0} = 197$ and 362 kJ/mol were determined for the NH_2 and NH molecules, respectively, on the basis of presumed consistency of the calculated values.

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