

A calculation of the photodetachment energy of NH_2^-

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The equation-of-motion (EOM) method was used to calculate the photodetachment energy of NH_2^- . An SCF level potential energy surface was calculated for NH_2 along the symmetric A_1 vibrational coordinates. Several points were also calculated on the asymmetric-stretch surface to provide a comparison with the symmetric-stretch surface. From these data, corresponding surfaces for NH_2 were obtained by adding the computed vertical detachment energy at each geometry. The calculated vertical photodetachment energy at the equilibrium geometry of NH_2 was 0.43 eV. By using experimental values for the vibrational energy difference between NH_2 and NH_2^- , the thermodynamic electron affinity of NH_2 was calculated to be 0.42 eV. From the computed potential energy surfaces, spectroscopic constants were calculated and compared to experimental results. The use of d functions on the nitrogen center was investigated and found to give little change in calculated ionization energies.

I. INTRODUCTION

The equation-of-motion (EOM) method has been successful in obtaining electron affinities in good agreement with experiment for diatomic molecules.¹⁻⁴ Polyatomic molecules represent the next step in implementation of the method, and, in particular, the NH_2^- photodetachment energy is a likely starting point for these studies. The NH_2^- ion is small enough to permit one to use a good quality basis set for the SCF calculation. Also, the photodetachment energy of this ion has been determined experimentally by several investigators.⁵ Moreover, other calculations are available which permit a comparison of total energies⁶⁻¹³ and orbital energies.^{6,14}

The orbital of NH_2^- from which the electron is removed is a nonbonding $1b_1$ lone pair orbital on the nitrogen. Experimental results for the NH_2^- photodetachment energy (to give the lowest state of NH_2) have been clustered around two values in recent years. During the late sixties, the accepted experimentally determined value was 1.2 eV.¹⁵ More recent results have been in the vicinity of 0.76 eV,⁵ while calculated values of the electron affinity of NH_2 have been lower than either of these experimental values. A recent calculation⁶ in which SCF energies were calculated for both NH_2 and NH_2^- gave an electron affinity that required a very large correlation correction to bring it into agreement with experiment. This fact indicates that any successful calculation must include some reasonable estimate of the electron correlation; such observations have also been made in our earlier work.¹⁻⁴

II. CALCULATION

The method used for these detachment energy calculations was the EOM technique developed by Simons *et al.*¹⁶ The SCF calculations were performed using the POLYATOM labels and integral programs and the RHF part of Goddard's GVB program which had been adapted for the Wright-Patterson Air Force Base CDC Cyber-74 computer by R. J. Blint. The basis set was obtained by adding diffuse functions to the s and p nitrogen functions reported by Dunning.¹⁷ Dunning's [5s 3p] contraction of Huzinaga's [9s 5p] Gaussian-type orbital basis

was used for nitrogen and his [2s] contraction (scaled to 1.2) of the [4s] basis was employed for hydrogen. The added diffuse functions had orbital exponents equal to $\frac{1}{4}$ of the value of the smallest exponent in the Huzinaga basis for the $p_x(b_2)$ and $p_y(a_1)$ orbitals (N.B., the molecule lies in the x, y plane, with the y axis being the C_2 symmetry axis). Two diffuse functions were added to the $p_x(b_1)$ symmetry orbital and one to the nitrogen s orbital. The b_1 and s orbital exponents were optimized to give the largest detachment energy (EOM level) at $R = 1.95$ bohrs and $\theta = 105^\circ$. When d functions were added to this basis, a lower total SCF energy was obtained for NH_2^- . However, these d orbitals did not improve the EOM detachment energy; therefore, they were not used in the final calculations of the potential surfaces. The resulting optimized basis set is shown in Table I. Most of the calculations on NH_2^- were performed for the symmetric A_1 geometry, however, a few calculations were performed on the asymmetric A' surface for comparison. For each geometry the EOM detachment energies were obtained for both the 2A_1 and the 2B_1 states of NH_2 . The orbital configuration corresponding to the 1A_1 state of NH_2^- is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 \ ^1A_1 .$$

From this configuration, the EOM method is used to study both states of NH_2 ,

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^1 \ ^2B_1$$

and

$$1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^2 \ ^2A_1 .$$

Most of the computer time required for these calculations is used in obtaining the SCF solution of NH_2^- and transforming the two-electron integrals to the MO basis. With these calculations completed, the EOM solution for the 2B_1 and 2A_1 ionization energies takes very little computer time.

III. RESULTS AND DISCUSSION

A. Potential energy surfaces for C_{2v} NH_2^- and NH_2

An SCF-level potential surface was calculated for NH_2^- using the optimized basis set discussed above. The

TABLE I. NH_2^- basis set.

| Center | Type | Exponent | Coefficient | |
|--------|--------|----------|-------------|----------|
| N | S | 5909.44 | 0.00624 | |
| | | 887.451 | 0.047669 | |
| | | 204.749 | 0.231317 | |
| | | 59.8376 | 0.788869 | |
| | | 19.9981 | 0.792912 | |
| | | 2.686 | 0.323609 | |
| | | 7.1927 | 1.0 | |
| | | 0.7000 | 1.0 | |
| | | 0.2133 | 1.0 | |
| | | 0.1066 | 1.0 | |
| | X | 26.786 | 0.038244 | |
| | | 5.9564 | 0.243846 | |
| | | 1.7074 | 0.817193 | |
| | | 0.5314 | 1.0 | |
| | | 0.1654 | 1.0 | |
| | | 0.0413 | 1.0 | |
| | | Y | 26.786 | 0.038244 |
| | | | 5.9564 | 0.243846 |
| | | | 1.7074 | 0.817193 |
| | | | 0.5314 | 1.0 |
| 0.1654 | 1.0 | | | |
| Z | 26.786 | 0.038244 | | |
| | 5.9564 | 0.243846 | | |
| | 1.7074 | 0.817193 | | |
| | 0.5314 | 1.0 | | |
| | 0.1654 | 1.0 | | |
| | 0.0625 | 1.0 | | |
| H | S | 19.2406 | 0.032828 | |
| | | 2.8992 | 0.231208 | |
| | | 0.6534 | 0.817238 | |
| | | 0.1776 | 1.0 | |
| | | | | |

energies of all geometries of NH_2^- were calculated without further optimization of the basis set. From this surface an equilibrium geometry of 1.95 bohrs for the bond length and 106° for the bond angle was obtained, at which the SCF energy was -55.51208 hartrees. The optimum geometry was obtained by a least-squares fit of the computed data points to a parabola. The energies of some previously reported calculations on NH_2^- together with corresponding geometries are given in Table II for comparison. An experimental geometry determination taken from x-ray work on KNH_2 gives values of 1.95 bohrs and 104° for the bond length and angle.¹⁸

To obtain a potential energy surface for the 2B_1 state of NH_2^- , the calculated EOM detachment energy was

added to the NH_2^- energy at each point on the surface as described in Eq. (1)

$$E_{\text{NH}_2}(r, \theta) = E_{\text{NH}_2^-}(r, \theta) + E_{\text{V.D.}}, \quad (1)$$

where $E_{\text{V.D.}}$ is the vertical detachment energy, and $E_{\text{NH}_2}(r, \theta)$ and $E_{\text{NH}_2^-}(r, \theta)$ are the total energies of NH_2 and NH_2^- , respectively, as functions of bond length and bond angle.

The potential surface for NH_2 , which is needed to obtain the thermodynamic electron affinity of NH_2 , calculated using this method could, at best, be described as an SCF-level surface. The change in correlation energy from the ion to the neutral species and the relaxation energy calculated by the EOM method should be small compared to the SCF energy. The resulting surface thus should simulate an SCF surface. Previously calculated SCF-level potential surfaces can be used to assess the quality of this surface. As a result of using Eq. (1), the equilibrium angle was larger and the total energy was higher than predicted by some recent SCF calculations on NH_2 (see Table III). Our total "simulated SCF" energy of NH_2 at the equilibrium geometry is -55.49689 hartrees, with $R = 1.92$ bohrs and $\theta = 107^\circ$. The NH_2 and NH_2^- surfaces are shown in Figs. 1 and 2. It should be mentioned that in carrying out these studies, we encountered one consistent irregularity in the NH_2 potential surface at 111° , which we do not yet fully understand. It can be seen from the similarities in the bond lengths and bond angles of the neutral and anion ($\Delta R = 0.03$ bohrs and $\Delta\theta = 1^\circ$) that the ground states of the two species should have very large overlap of their vibrational wavefunctions. Franck-Condon coefficients which we have computed using harmonic functions support this conclusion.

B. Spectroscopic parameters

The four valence force constants were calculated for both NH_2 and NH_2^- by least-squares fitting a parabola to the appropriate potential curve (symmetric or asymmetric stretch and bend) which, of course, makes the assumption of harmonic behavior. The off-diagonal force constant, $K_{r\alpha}$, was determined from Eq. (2), once the other force constants had been computed from symmetric and asymmetric stretch data and pure bending data.

$$\Delta E = K_r r^2 + \frac{1}{2} K_\alpha \alpha^2 \pm K_{r\alpha} r \alpha + 2K_{\alpha r} \alpha r. \quad (2)$$

In Eq. (2), r is the N-H bond length stretch, α is the HNH angle displacement; the + sign holds for a symmet-

TABLE II. Some results of calculations for NH_2^- .

| | Heaton <i>et al.</i> (Ref. 6) | Czimadia <i>et al.</i> (Ref. 8) | Csizmadia <i>et al.</i> (Ref. 7) | This work |
|-------------------------------|----------------------------------|------------------------------------|-------------------------------------|--|
| R_{NH} (bohrs) | 1.9 | 1.918 | 1.962 | } experi- mental values for NH_3 |
| θ_{HNH} (deg) | 102.5 | tetrahedral | 107 | |
| E_{total} (hartrees) | -55.512591 | -55.5210 | -55.5009 | -55.51208 |

TABLE III. Some results of calculations for NH_2^- .

| | Brown <i>et al.</i> (Ref. 11) (minimal base) | Bender <i>et al.</i> (Ref. 9) (SCF) | Krauss (Ref. 10) | Claxton (Ref. 12) | Pople <i>et al.</i> (Ref. 13) | This work |
|-------------------------------|--|---|---------------------|----------------------|----------------------------------|--------------|
| R_{NH} (bohrs) | 2.04 | 1.90 | 1.95 | 2.0 | | 1.92 |
| θ_{HNH} (deg.) | 108 | 105 | 107.5 | 105 | 104.3 | 107 |
| E_{total} (hartrees) | -55.3752 | -55.5757 | -55.454 | -55.5260 | RHF -55.57273 | -55.49689 |
| | | | | | UHF -55.57703 | |

ric stretch, the - sign for an asymmetric stretch. Using the resulting force constants, the fundamental vibrational frequencies were obtained by using the valence force equations of Ref. (19), the results of which are shown in Table IV. These calculations show that the SCF potential curve for NH_2^- gives reasonably good vibrational frequencies. The corresponding values for NH_2 indicate that the NH_2 potential surface is not of high quality.

C. Photodetachment energy of NH_2^-

The calculated EOM-level photodetachment energy of NH_2^- is 0.43 eV; this value does not take into consideration the vibrational levels in the NH_2^- and NH_2 potential surfaces. The vertical electron affinity for NH_2 (also without consideration of vibrational levels) is 0.40 eV. The thermodynamic electron affinity determined using Eq. (3) with experimentally determined vibrational energies is 0.42 eV:

$$E. A. (\text{thermo.}) = E_{\text{NH}_2}(R_e, \theta_e) - E_{\text{NH}_2^-}(R_e^-, \theta_e^-) + \frac{\hbar}{2} \left(\sum_i \nu_i^{\text{NH}_2} - \nu_i^{\text{NH}_2^-} \right). \quad (3)$$

Using the frequencies calculated from the above potential surfaces, rather than the experimental vibrational frequencies, gives a thermodynamic electron affinity of 0.45 eV, which agrees with the Koopmans' theorem-level value reported by Heaton *et al.*⁶ (0.36 eV). A CNDO calculation of Zahradnik and Carsky²² gave a Koopmans' theorem result of 0.37 eV. The Δ SCF work of Heaton⁶ resulted in an electron affinity of -1.705 eV which, after corrections for correlation, was increased to 0.30 eV. Recent experimental values are significantly higher than any of the above theoretical predictions (Brauman *et al.*, 0.744 ± 0.022 eV; Feldmann, 0.76 ± 0.04 eV; and Celotta *et al.*, 0.779 ± 0.037 eV)⁵; possible reasons for this discrepancy are discussed below.

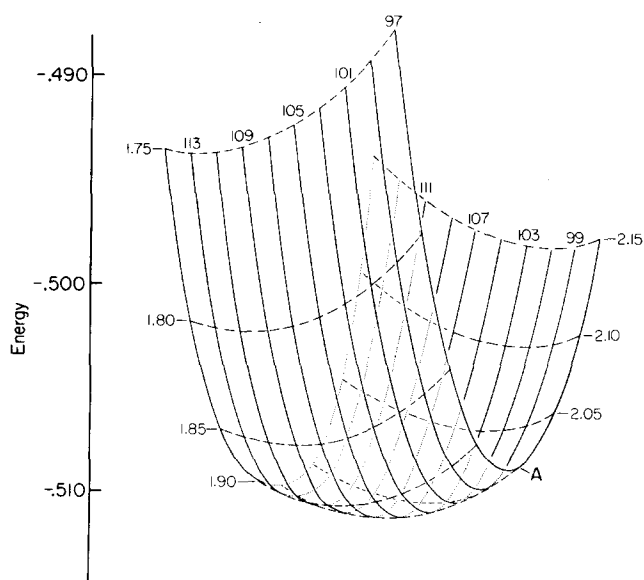


FIG. 1. The SCF calculated potential surface of NH_2^- . The energy is in hartrees (55 hartrees are added to each point); the angles (indicated at the top of the figure) are in degrees; and the N-H distances (indicated at the side of the figure) are in bohrs. On the side of the surface marked A, the 1.95 bohr representation obscures the 2.00 bohr representation, (both can be seen on the other side). The curve not identified on the figure is at an angle of 115° .

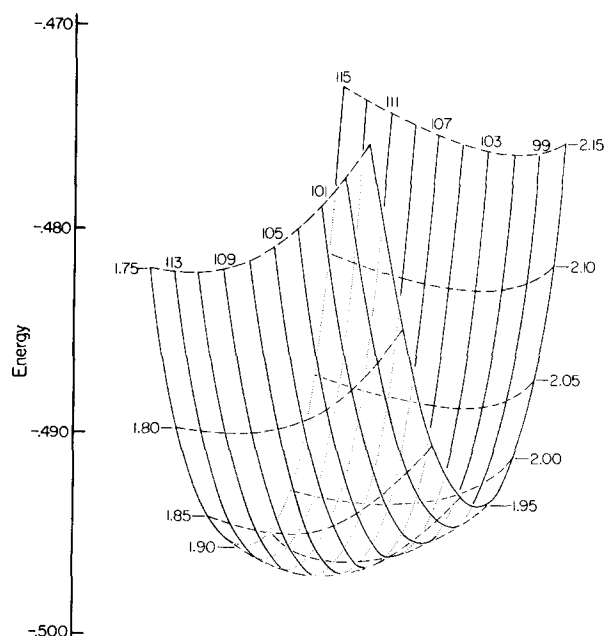


FIG. 2. The calculated potential surface of NH_2 . The energy is in hartrees (55 hartrees are added to each point); the angles (indicated at the top of the figure) are in degrees; and the N-H distances (indicated at the side of the figure) are in bohrs. The curve not identified on the figure is at an angle of 97° .

TABLE IV. Spectroscopic parameters.

| | This work | | Brown <i>et al.</i> (Ref. 11) | Exptl. | |
|---|-------------------------|-------------------------|----------------------------------|-------------------------|--------------------------|
| | NH_2 | NH_2^- | NH_2 | NH_2 (Ref. 20) | KNH_2 (Ref. 21) |
| $Kr \left(\frac{\text{mdyn}}{\text{\AA}} \right)$ | 7.256 | 6.45 | 6.95 | | 5.724 |
| $Krr \left(\frac{\text{mdyn}}{\text{\AA}} \right)$ | -0.606 | -0.085 | | | -0.112 |
| $K\alpha \left(\frac{\text{ergs}}{\text{rad}^2} \right)$ | 9.324×10^{-12} | 7.27×10^{-12} | 1.14×10^{11} | | 7.55×10^{-12} |
| $k\alpha r \left(\frac{\text{dyn}}{\text{rad}} \right)$ | -5.965×10^{-4} | -3.376×10^{-4} | | | -3.13×10^{-4} |
| ν_1 (cm^{-1}) | 3541 | 3421 | | | 3212.5 |
| ν_2 (cm^{-1}) | 1655 | 1523 | | 1497.5 | 1539.5 |
| ν_3 (cm^{-1}) | 3815 | 3477 | | | 3263.0 |
| R (bohrs) | 1.92 | 1.95 | 2.04 | 1.936 | 1.95 ^a |
| θ (deg) | 107 | 106 | 101.8 | 103.4 | 104 ^a |

^aJuza *et al.*, Ref. 18.

D. Comments on the vertical photodetachment to the 2A_1 state

The vertical photodetachment energy was also calculated at the equilibrium geometry of NH_2^- for the 2A_1 state with the basis which was optimized for the 2B_1 state. This geometry is far from equilibrium for the 2A_1 state ($R_e = 1.90$ bohrs and $\theta_e = 144^\circ$),²⁰ however the results of this calculation show some interesting trends. At an angle of 106° , the splitting between the 2A_1 and 2B_1 states of NH_2 changes by only 0.14 eV with a 0.4 bohr change in bond length. This indicates the potential energy surface of the 2A_1 state, in the neighborhood of the equilibrium angle of the 2B_1 state (which corresponds to an excited bending of the 2A_1 state), is similar in shape to the 2B_1 surface as the bond lengths are varied. This observation is supported by the experimentally determined surfaces which show a change in bond length of only 0.02 \AA ²⁰ in going from the equilibrium geometry for the 2B_1 state to the 2A_1 state equilibrium geometry. Further supporting evidence is found in the flash photolysis spectra of Dessler and Ramsay²³ who assign a vibrationally excited series (bending vibration) in the 2B_1 - 2A_1 spectrum. Using the EOM-computed vertical detachment energy of 2.25 eV for the 2A_1 state at $R = 1.92$ and $\theta = 107$, together with the previously discussed 2B_1 detachment energy, the excitation energy for the $^2B_1 \rightarrow ^2A_1$ transition is calculated to be 1.84 eV, which is in reasonable agreement with the results of Dressler and Ramsay who report the most intense part of their spectrum to lie between 1.98 and 2.4 eV.²³

IV. CONCLUSION

From a potential energy surface along both the symmetric and asymmetric stretch coordinates, we obtain a vertical detachment energy for NH_2^- of 0.42 eV using the experimental vibrational frequencies. This gives a value that is approximately 55% of the current experi-

mental results. The calculated excitation energy for the $^2B_1 \rightarrow ^2A_1$ transition is within 0.2 eV of the experimentally observed value. The addition of d functions to the basis set for the NH_2^- SCF calculation does not improve the detachment energy. It was observed by Heaton⁶ and by ourselves in the NH_2 - NH_2^- system that d functions seem to lower the energy of both the parent and daughter by nearly equal amounts.

In the particular case considered here, the difference between the calculated and experimental results for the electron affinity in NH_2 is larger than those found in our earlier studies of diatomics. Thus, our (good) results for diatomics may be fortuitous, or calculations of accurate electron detachment energies of NH_2^- as well as diatomics may require extensive configuration interaction treatment, larger basis sets, or an extension of the present EOM method to higher order. Because our diatomic calculations employed Slater type orbitals, whereas this work used Gaussian type orbitals, part of the reason for the large experimental-theoretical discrepancy may be due to the inadequacy of our Gaussian basis. It is not really clear how to efficiently use Gaussian functions to describe the diffuse electron density of our anion. This problem is deserving of more work.

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