

tion among the membranes, they will occasionally stick together in close contact over some extended regions. At the boundary they will in general depart tangentially forming a line of cusp singularities. If, for example, the membranes form flexible spheres as in vesicles or some microemulsions, an attraction may lead to dimers<sup>5</sup> having a finite contact area. Such lines of cusp singularities produce in bulk scattering a term  $\sim q^{-(4+1/2)}$  and in surface scattering a term  $\sim q^{-(2+1/2)}$  in addition to the Porod terms  $\sim q^{-4}$  and  $q^{-2}$ . The coefficients are  $-2\pi^{3/2}(L/V)\langle |k_1 - k_2|^{-1/2} \rangle$  and  $2\pi^{3/2}(L/V)\langle |k_1 - k_2|^{-1/2} \rangle$ , respectively, where  $L$  is the

length of the singularity line  $L$ ,  $\langle \rangle$  is the average along  $L$ , and  $k_1, k_2$  are the sectional curvatures normal to  $L$  of the two surfaces which join tangentially at  $L$ .

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## NH<sub>2</sub> electron affinity

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We report the electron affinity of amidogen (NH<sub>2</sub>), the amino radical, obtained from the photoelectron spectrum of the amide ion (NH<sub>2</sub><sup>-</sup>). The literature electron affinity values from early laser photodetachment experiments have relatively large uncertainties: EA(NH<sub>2</sub>) = 0.744 ± 0.022 eV from photodetachment threshold measurements<sup>1</sup> and EA(NH<sub>2</sub>) = 0.779 ± 0.037 eV from photoelectron spectroscopy.<sup>2</sup> The development of higher resolution (5–25 meV) negative ion photoelectron spectrometers<sup>3–6</sup> now permits a significantly improved determination of the electron affinity as well as the observation of more detailed structure in the photoelectron spectrum. The spectrum reported here shows clear rotational bands in the photodetachment of NH<sub>2</sub><sup>-</sup>. Partially resolved rotational band structure has been observed previously in photoelectron spectra<sup>5,7</sup> of small hydride ions such as OH<sup>-</sup>, OD<sup>-</sup>, SH<sup>-</sup>, SD<sup>-</sup>, and CH<sub>2</sub><sup>-</sup>.

The photoelectron spectrometer used in this experiment has been described in detail previously.<sup>5</sup> NH<sub>2</sub><sup>-</sup> is produced by introducing ammonia into a helium flow downstream of a microwave discharge; a beam of about 10 pA was achieved. Negative ions are extracted from the flow tube, mass selected with a Wien velocity filter, and crossed with a continuous 363.8 nm (3.408 eV) laser beam of fixed photon energy at a power of 40 W in an optical build-up cavity.<sup>8</sup> The kinetic energy of photodetached electrons is measured by a hemispherical electrostatic analyzer.<sup>5</sup> The absolute electron kinetic energy (eKE) is calibrated with O<sup>-</sup> ions, EA(O) = 1.461 125 ± 0.000 001 eV,<sup>9</sup> and the energy scale compression factor<sup>5</sup> of 0.6% is determined from photodetachment of W<sup>-</sup>. The uncertainty of the eKE scale is ± 5 meV and the instrumental linewidth is 8–9 meV. The rota-

tional temperature of OH<sup>-</sup> ions produced in this source under similar conditions is 315 ± 20 K, and the vibrational temperatures are typically 300–500 K.<sup>8</sup>

Figure 1 shows the NH<sub>2</sub>( $\tilde{X}^2B_1, v' = 0$ ) ← NH<sub>2</sub><sup>-</sup>( $\tilde{X}^1A_1, v'' = 0$ ) vibrational origin transition in the photoelectron spectrum of NH<sub>2</sub><sup>-</sup>. We also observed transitions in the symmetric stretch NH<sub>2</sub>( $v'_1 = 1$ ) ← NH<sub>2</sub><sup>-</sup>( $v''_1 = 0$ ) and in the bend NH<sub>2</sub>( $v'_2 = 1$ ) ← NH<sub>2</sub><sup>-</sup>( $v''_2 = 0$ ) which had intensities of 0.5% and 0.9% respectively relative to the vibrational origin. Weak transitions to the  $\tilde{A}^2A_1$  state<sup>10</sup> of NH<sub>2</sub> were observed at electron kinetic energies below 1.5 eV. The rotational contour of the origin transition shows *Q*, *P*, and *R* branches. The *Q* branch has a FWHM of 8.5 meV, limited by the instrumental resolution. The rotationless origin is found from the rotational modeling to be within 1 meV of the center of the *Q* branch and this yields the electron affinity EA(NH<sub>2</sub>) = 0.771 ± 0.005 eV. This value for EA(NH<sub>2</sub>) falls within the range of the previous experimental determinations.<sup>1,2</sup> A recent theoretical value<sup>11</sup> is EA(NH<sub>2</sub>) = 0.707 eV. We also measured the angular distribution of the ejected electron with the laser operating on the 351 nm line. This showed anisotropic detachment with asymmetry parameter  $\beta$  of 0.34 ± 0.05. Within experimental error the *Q*, *P*, and *R* branches all had the same angular distribution.

The ground electronic state of the amino radical is formed by removing an electron from the nonbonding *b*<sub>1</sub> orbital of NH<sub>2</sub><sup>-</sup>. The resulting small geometry change upon photodetachment is reflected by the narrowness of the *Q* branch and by the weak intensities of higher vibrational transitions. The observed vibrational transitions were totally consistent with the known experimental molecular geome-

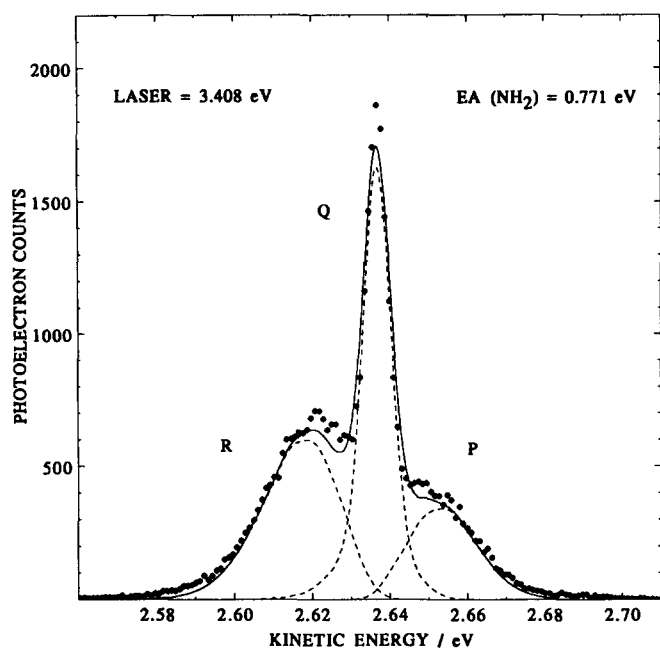


FIG. 1. Photoelectron spectrum of  $\text{NH}_2^-$  at a photon energy of 3.408 eV. The photoelectron counts are plotted vs the measured center-of-mass electron kinetic energy. Experimental data are represented by points; the line is the simulation of the rotational band contour described in the text. The individual P, Q, and R branches are shown by dashed lines.

tries<sup>12,13</sup> and vibrational frequencies,<sup>14–16</sup> for the anion and neutral species. At the estimated anion vibrational temperature, the influence of unresolved sequence bands on the position of the origin band is negligible. The angular distribution in the photodetachment of  $\text{NH}_2^-$  at 488 nm is isotropic<sup>2</sup> with a  $\beta$  of  $0.027 \pm 0.012$  in contrast to our value of 0.34 at 351 nm. Since the detached electron is similar to an atomic  $p$  electron it will depart as an asymptotic  $s$  or  $d$  wave. The  $d$  electron is strongly suppressed near threshold<sup>17</sup> but as the photon energy is raised it becomes increasingly important. This causes a change of  $\beta$  from zero and is demonstrated in the differences in  $\beta$  at 488 and 351 nm. Despite the nonzero value of  $\beta$  at 351 nm we shall model the detachment process as being dominated by  $s$ -wave detachment. The validity of this assumption is corroborated by a lack of extra rotational branches. Furthermore, since the three rotational branches have, within experimental error, identical  $\beta$  values, we can assume that their relative intensities are not strongly dependent upon the angular momentum state of the continuum electron and thus can be modeled by  $s$ -wave detachment.

The photodetachment transition is modeled as a two step process,  $\text{NH}_2^-(\tilde{X}^1A_1) + h\nu \rightarrow [\text{NH}_2^-]^*(^1B_1) \rightarrow \text{NH}_2(\tilde{X}^2B_1) + e(ks)$ . The symmetry of the putative intermediate state, which represents an amide ion with the extra electron in a continuum orbital, is fixed by the selection rules<sup>10</sup> for a bound-bound transition and by correlation with the final neutral state plus an  $s$  wave. For the initial  $^1B_1 \leftarrow ^1A_1$  absorption, the transition moment lies parallel to the  $c$  axis (perpendicular to the plane of the molecule) and hence type C selection rules<sup>10</sup> are applicable:  $\Delta J = 0, \pm 1, \Delta K_a = \pm 1$ , and  $\Delta K_c = 0$ . The rotational energy levels of  $\text{NH}_2$  and  $\text{NH}_2^-$

are determined by directly solving the asymmetric rotor Hamiltonian<sup>18</sup> using known rotational constants.<sup>12,13</sup> The intensity of each line is calculated from the Boltzmann population of the  $\text{NH}_2^-$  level at the estimated rotational temperature of 320 K and appropriate Hönl–London factors.<sup>10,18</sup> The calculated lines are then broadened by Gaussians with the instrumental linewidth of 8 meV and the resulting spectrum is included in Fig. 1. A Gaussian profile is chosen as it closely reproduces the line shape of detachment from atomic anions such as  $\text{O}^-$  and  $\text{W}^-$ . The shape of the simulated contour agrees with the measured spectrum within experimental error.

Thermochemical quantities of interest may be derived from the electron affinity measured here. The heat of formation of  $\text{NH}_2^-$  is given by  $\Delta H_{f,0\text{K}}^\circ(\text{NH}_2^-) = \Delta H_{f,0\text{K}}^\circ(\text{NH}_2) - \text{EA}(\text{NH}_2)$ . Taking  $\Delta H_{f,0\text{K}}^\circ(\text{NH}_2) = 45.8 \pm 0.3$  kcal/mol from recent photoionization experiments,<sup>19</sup> this yields  $\Delta H_{f,0\text{K}}^\circ(\text{NH}_2^-) = 28.0 \pm 0.4$  kcal/mol. The gas phase acidity of ammonia is obtained from  $\Delta H_{a,0\text{K}}^\circ(\text{NH}_3) = D_0(\text{H}-\text{NH}_2) + \text{IP}(\text{H}) - \text{EA}(\text{NH}_2)$ . Using the ionization potential<sup>20</sup>  $\text{IP}(\text{H}) = 313.59 \pm 0.01$  kcal/mol and the ammonia dissociation energy<sup>19</sup>  $D_0(\text{H}-\text{NH}_2) = 106.7 \pm 0.3$  kcal/mol, we derive  $\Delta H_{a,0\text{K}}^\circ(\text{NH}_3) = 402.5 \pm 0.4$  kcal/mol, in good agreement with the gas phase equilibrium value<sup>21</sup> of  $\Delta H_{a,298\text{K}}^\circ(\text{NH}_3) = 403.6 \pm 0.8$  kcal/mol.

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