Molecular-beam study of the ammonia–noble gas systems: Characterization of the isotropic interaction and insights into the nature of the intermolecular potential

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We report new high resolution molecular beam experiments aimed at characterizing the intermolecular interaction in the NH3–Ng (Ng = He, Ne, Ar, Kr, Xe) weakly bound complexes. Integral cross section data are obtained over a sufficiently wide velocity range and with rotationally hot NH3 molecules to produce (except for the NH3–He case) a well resolved “glory” quantum interference pattern. Data analysis, carried out by employing a recently proposed potential model, allows unique information on the absolute scale of the intermolecular interaction to be obtained both at long range and at the equilibrium distance. An extensive and internally consistent comparison with the behavior of the corresponding Kr–Ng systems is exploited in order to identify those cases where an interaction component due to charge transfer effects provides an appreciable intermolecular bond stabilization that is clearly distinct from and must be added to the standard van der Waals plus induction picture. The results of the present investigation extend the phenomenology of perturbative charge transfer effects in gas phase complexes involving hydrogenated molecules. © 2011 American Institute of Physics. [doi:10.1063/1.3660199]

I. INTRODUCTION

The detailed characterization of intermolecular potentials and the development of suitable analytical functions for their formulation provide the foundation on which microscopic and macroscopic properties of matter can be described and extensive molecular dynamics simulations can be built.1 Specifically, the study of the intermolecular interaction between hydrogenated molecules and neutral species is of great interest for understanding presence and role of hydrogen bonding in various environments.2 This goal can be achieved by coupling detailed experimental and theoretical information, for prototypical and relative simple molecule–atom and molecule–molecule systems.

Recently, we have carried out molecular beam scattering experiments on water and hydrogen sulphide molecules interacting with noble gas atoms3–7 and other simple molecules (O2, N2, H2, CCl4, CF4)8–10 in order to measure, under high angular and velocity resolution conditions, the total (elastic + inelastic) integral cross section Q as a function of the collision velocity v. The Q(v) data have been obtained in an absolute scale and resolving the “glory” oscillations due to quantum interference effects. Such data, measured and analyzed with consistent methodologies, provided unique information on the absolute scale of the intermolecular interaction both at long and at intermediate distance range (i.e., near the equilibrium distance). The comparison of the experimental results with predictions of correlation formulas,11,12 valid for van der Waals interactions (here defined for our convenience as the combination of size repulsion plus dispersion attraction) perturbed by induction contributions, has enabled us to identify from a phenomenological point of view those systems for which an additional interaction component (namely, charge transfer (CT)) is operative.4,5,7,8,10 In parallel, accurate ab initio calculations have also been carried out both to enable the detailed characterization of the potential energy surfaces5,10,13,14 and to determine the modification of the electronic charge distributions as a function of the intermolecular distance, and for various relative orientations of interacting partners.5,10,13,14 Such calculations provided us a robust theoretical explanation of the origin of the experimental findings and also clarified the stereo-specificity of such additional CT component, considered now a characteristic feature of hydrogen-bonded complexes.2

Indeed, the characterization of other intermolecular complexes, such as, for example, those involving ammonia, is necessary in order to extend the phenomenology of CT in weakly interacting intermolecular complexes. Ammonia–noble gas (NH3–Ng) systems have been the target of several previous studies, most of which are theoretical investigations.15 Motivations of such studies include the effect of the intermolecular potential on the ammonia spectra, on the pressure broadening coefficients,16 and on those features arising from ammonia “umbrella” (or inversion) motion.15,17 Direct experimental probes of the characteristics of the ammonia-noble gas complexes mostly came from spectroscopic investigations, performed in the far infrared and microwave region.18

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Few scattering measurements are reported in literature and regard essentially differential and integral inelastic cross sections,19–21 which have been demonstrated to be scarcely affected by the umbrella motion,22 and total (elastic + inelastic) differential cross sections.23 However, experimental data directly probing the absolute scale of the intermolecular interaction are lacking. Only few data and in a narrow temperature range are available for the second virial coefficient.24 Therefore, it appears to be crucial to obtain further information on such systems in order to discover trends, regularities, and changes along the whole family of ammonia–noble gas systems and to compare the observations with the behavior of aggregates involving other hydrogenated molecules (see for instance Ref. 25).

The present paper reports novel scattering experiments on the NH3–Ng systems (Ng = He, Ne, Ar, Kr, Xe) performed in our laboratory to measure the total integral cross section $Q(v)$ in a sufficient wide range of collision velocity $v$ in order to observe a well resolved glory interference effect overlapped to a monotonically decreasing average component. Such experiments have been carried out by using the same methodology previously exploited to investigate the interaction of water and hydrogen sulphide molecules with other closed shell neutral species.3–9 Under the present experimental conditions, namely, rotationally hot molecular beams and thermal collisional energy range, the umbrella motion of NH3 is expected to be ineffective for the scattering observable of interest here.25 The main reason is its time scale (about $10^{-11}$ s) (see Refs. 18 and 26) much longer than the average rotation ($10^{-13}$ s) and collision ($10^{-12}$–$10^{-13}$ s) times.5 Second, the measured scattering cross section depends on the weighted sum of contributions at intermediate and large collision angular momentum.5,27

Section II provides a short description of the experimental apparatus and shows the measured $Q(v)$ data. Their analysis and the obtained interaction potentials are given in Sec. III. A discussion focused on the internal comparison of potential features is performed in Sec. IV. Some conclusions follow in Sec. V.

II. EXPERIMENTAL APPARATUS

The experimental apparatus used to carry out the scattering measurements consists of a set of differentially pumped vacuum chambers connected by slits for the molecular beam (MB) collimation. The MB emerges through a nozzle (1 mm in diameter) from a source which can operate under nearly effusive or moderately supersonic conditions. After mechanical velocity selection, the MB crosses a scattering chamber, which is continuously filled ($\approx 10^{-3}$ mbar) with the target gas and evacuated ($\approx 10^{-6}$ mbar) by an automated procedure. After the scattering region, the on-line MB intensity is detected by an electron bombardment ionizer followed by a quadrupole mass analyzer. All the geometrical characteristics and details of the apparatus are given in Ref. 28. Ammonia MBs have been generated by expanding ammonia vapors through a nozzle heated to 500–600 K in order both to suppress cluster formation and to “heat up” the rotational motion of molecules. NH3 vapors have been kept in the source both pure, at a stagnation pressure of 5–6 mbar, and in a mixture with He, always at low total stagnation pressure, in order to extend the probed collision velocity range by shifting the MB velocity distribution (see Fig. 1). MB velocity analysis and selection have been achieved by the use of a slotted disk velocity selector with a high resolution (full width at half maximum less than 5%).

At each selected MB velocity $v$, the measurement of MB attenuation $I/I_0$ (where $I$ and $I_0$ represent the MB intensity with and without target gas in the scattering chamber, respectively) permits the determination of the integral cross section $Q(v)$ through the Lambert-Beer law

$$Q(v) = -\frac{1}{NL} \log \frac{I}{I_0},$$

where $N$ is the gas target density and $L$ is the effective length of MB path in the scattering chamber. The scattering chamber, filled with noble gas at a pressure in the $10^{-3}$–$10^{-4}$ mbar range, has been kept at the liquid air temperature (about 90 K) in order to enhance the velocity resolution of the experiments. As previously,3–7 the absolute values of $Q(v)$ have been obtained by an internal calibration of the $NL$ factor, based on the direct measurement of the gas flow in the scattering chamber29 and on the absolute values of the He–Ar cross section.30

As stressed before, MBs used in the present investigation contain rotationally “hot” molecules showing an average rotational period comparable or shorter than the typical collision time in our experiments.28,31 Therefore, the molecules rotate sufficiently fast during each collision to exploit essentially elastic events, mostly driven by the average (isotropic) interaction component.4,5,32

III. RESULTS AND DATA ANALYSIS

Measurements have been performed for the complete NH3–Ng family of systems (Ng = He, Ne, Ar, Kr, Xe) in a wide range of MB velocity. The experimental integral cross section results are plotted in Fig. 2. In the semiclassical approximation $Q(v)$ can be written as sum of two contributions

$$Q(v) = \tilde{Q}(v) + \Delta Q(v),$$

FIG. 1. Velocity distributions measured by using in MB source pure NH3 vapor and NH3–He gaseous mixture in the 1:1 ratio.
termolecular distance \( r \) of the intermolecular potential \( \Delta Q_1 \) where Fig. 2. Integral cross section \( Q \) for NH\(_3\)-Ng scattering plotted as a function of the selected MB velocity \( v \). Symbols are the experimental data and lines are the fit using the ILJ potential model.

where \( \Delta Q(v) \) is an oscillatory term due to the glory quantum interference effect while \( \bar{Q}(v) \) is the average monotonic component. \( Q(v) \) shows a monotonic behavior for NH\(_3\)-He, while for all the other systems it exhibits a well resolved oscillatory pattern due to the glory effect over-imposed to a smooth component of the cross section. As stressed above, the scattering cross section is an extremely sensitive probe of the interaction potential. In particular, the glory structure is sensitive to the intermediate-range interaction (the potential well region), while \( \bar{Q}(v) \) probes mainly a defined interval of the long-range region\(^{27} \) (see also below).

The analysis has been carried out by exploiting a recently proposed potential function, the improved Lennard-Jones (ILJ) model,\(^{27} \) which provides an accurate description of the intermolecular potential \( V(r) \) in a wide range of the intermolecular distance \( r \). Such model also permits a consistent comparison of different systems, being \( V(r) \) generated by only few scaling parameters. The ILJ functional form is the following:

\[
V(r) = \varepsilon \left[ \frac{6}{n(r)-6} \left( \frac{r_m}{r} \right)^{6} - \frac{n(r)}{n(r)-6} \left( \frac{r_m}{r} \right)^{6} \right].
\]

where

\[
n(r) = \beta + 4 \left( \frac{r}{r_m} \right)^{2}.
\]

In Eq. (3), the first term represents the repulsion while the second one represents the attraction. \( \varepsilon \) defines the well depth, \( r_m \) is the equilibrium distance, and \( \beta \) determines the shape (reduced force constant) of the potential in the region of the well. This parameter varies in a limited range (i.e., from 9 for rare gas dimers to 7 for halide ions interacting with closed shell particles).

As for water–Ng (Ref. 5) and hydrogen sulphide–Ng (Ref. 7) families we use \( \beta = 9 \), a value typical of the weak intermolecular interactions between neutral closed shell species.\(^{27,33} \) Note also that the choice of a \( \beta \) value slightly smaller that 9 does not provide appreciable changes in the obtained best fit \( \varepsilon \) and \( r_m \) parameters. Therefore, during the fitting procedure only \( \varepsilon \) and \( r_m \) have been varied, to properly reproduce extrema position, amplitude, and frequencies of \( \Delta Q(v) \) and the absolute value of \( Q(v) \), the latter within the uncertainty of its calibration (3–4\%). The ILJ formulation has been demonstrated to adequately describe potential well, intermediate, and long range attraction for both isotropic and anisotropic neutral and ionic systems (see Ref. 27 and references therein). Indeed the ammonia-rare gas interactions are anisotropic but under the present experimental conditions (rotationally hot molecules) the experimental data are sensitive to the spherically averaged potential. Therefore, the use of the ILJ two-body function in the fit of the experimental data allows us to extract the orientationally averaged interaction parameters both in the well (\( \varepsilon \) and \( r_m \)) and at long range (\( C_6 = \varepsilon r_m^6 \)). The latter can also be expressed in terms of long-range dispersion and induction components, as \( C_6 = C_{\text{disp}} + C_{\text{ind}} \). For the NH\(_3\)-Ng systems, an evaluation of the \( C_{\text{disp}} \) values is possible by using the semi-classical relation \( C_6 = 1.04 \times C_{\text{disp}} \). The numerical coefficient 1.04 has been obtained by considering the relative role of induction, arising from the average attraction between permanent dipole of ammonia (1.47 D (Ref. 34)) and induced dipole on Ng, with respect to dispersion.\(^{1,5,11,12,35} \)

The cross sections \( Q(v) \), calculated in the center of mass frame using the JWKB method,\(^{4} \) are convoluted in the laboratory system for a direct comparison with the measured data. The convolution includes the average over the thermal motion of the target gas, evaluated at the temperature of the scattering chamber, the transmission function of the velocity selector, and a small correction to \( Q(v) \) due to the finite angular resolution of the apparatus (the so called “limit angle” correction, due to the uncertainty principle).\(^{38} \) Such correction takes into account also the slit dimensions and distances, defining MB collimation, the mass of the projectile, the cross section, and the probed velocity values.

The best fit \( \varepsilon \) and \( r_m \) parameters are given in Table I, while Fig. 2 compares calculated and measured cross sections, showing an excellent accord between the two. This
TABLE I. Well depth $\varepsilon$ (meV) and equilibrium distance $r_m$ (Å) for the NH$_3$–Ng systems (estimated uncertainty 3–5% for $\varepsilon$, 1–2% for $r_m$, and 2–4% for the $\varepsilon r_m$ product). Predictions of correlation formulas$^{11}$ (estimated uncertainty 10% for $\varepsilon$ and 3% for $r_m$) and values obtained for the Kr–Ng systems$^{27,36}$ are also reported for comparison.

<table>
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<tr>
<th>System</th>
<th>Experimental</th>
<th>Predictions</th>
<th>Kr–Ng</th>
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<tr>
<td></td>
<td>$\varepsilon$</td>
<td>$r_m$</td>
<td>$\varepsilon$</td>
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<tr>
<td>NH$_3$–He</td>
<td>2.45</td>
<td>3.70</td>
<td>2.77</td>
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<td></td>
<td>2.26$^a$</td>
<td>3.67$^a$</td>
<td></td>
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<td>NH$_3$–Ne</td>
<td>5.55</td>
<td>3.67</td>
<td>5.66</td>
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<tr>
<td>NH$_3$–Ar</td>
<td>13.6</td>
<td>3.83</td>
<td>12.7</td>
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<tr>
<td>NH$_3$–Kr</td>
<td>17.7</td>
<td>3.94</td>
<td>15.7</td>
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<tr>
<td>NH$_3$–Xe</td>
<td>21.5</td>
<td>4.11</td>
<td>18.4</td>
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</table>

$^a$Average values.$^{19}$

TABLE II. $C_6$ and $C_{\text{disp}}$ coefficients, in eV Å$^6$, obtained as described in the text (see Sec. III) at different reduced values of the distance $x = r/r_m$. The $C_{\text{disp}}$ are compared with theoretical and experimental data from the literature$^{37,38}$ and with values for the Kr–Ng systems.$^{27}$ The estimated maximum uncertainty in the present long range coefficients is about 10%.

<table>
<thead>
<tr>
<th>System</th>
<th>$C_6$</th>
<th>$C_{\text{disp}}$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$x = 5$</td>
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<tr>
<td>NH$_3$–He</td>
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<td>6.29</td>
</tr>
<tr>
<td>NH$_3$–Ne</td>
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<td>NH$_3$–Ar</td>
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<tr>
<td>NH$_3$–Kr</td>
<td>70.1</td>
<td>66.2</td>
</tr>
<tr>
<td>NH$_3$–Xe</td>
<td>110</td>
<td>104</td>
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</tbody>
</table>

clearly supports the validity of analysis, carried out under the present experimental conditions by using the isotropic potential model, noting that, if the interaction anisotropy played a non-marginal role, we would have observed a quenching of the glory amplitude. Values of the long range attraction coefficients $C_6$ and $C_{\text{disp}}$ obtained as described above are given in Table II, where a comparison with data available from literature is also shown. The good agreement confirms again the accuracy of present analysis. Finally, the obtained potentials are plotted in Fig. 3 to emphasize regular interaction changes along the whole NH$_3$–Ng family.

IV. DISCUSSION

For NH$_3$–He the obtained $\varepsilon$ and $r_m$ values are within the uncertainty boundaries of previous experimental investigations$^{23}$ and compare very well with the isotropic component of the more recent determination of the PES.$^{19}$ For NH$_3$–He and NH$_3$–Ar systems the proposed spherical potentials have also been used to calculate the second virial coefficient $B(T)$ as a function of the temperature $T$. Computed coefficients, reported in Fig. 4, appear to exhibit values comparable, although systematically higher, with respect to the experimental ones.$^{19,24}$

The comparison remarks that a spherical isotropic potential is not sufficient to describe $B(T)$ at low temperature where the interaction anisotropy may play a non-negligible role for the present systems. It is well known that the inclusion in the calculations of the interaction anisotropy will add a negative contribution to $B(T)$, in particular a low temperature.$^1$ This provides a substantial better agreement with the experimental data, as shown in Ref. 19.

Hereafter, the discussion of the NH$_3$–Ng systems is based on an extensive comparison with the behavior of Kr–Ng systems, for which data of the same type are available: most of them have been recently analyzed$^{27}$ by using the present potential model. This choice is motivated by the similar polarizabilities of Kr (2.49 Å$^3$) and NH$_3$ (2.16 Å$^3$)$^{34,37}$ It is important to remember that the polarizability is the basic property affecting non-covalent intermolecular potential features and particularly those of the van der Waals component. Indeed, correlation formulas based on the polarizability of interacting partners,$^{11,12}$ predict the $\varepsilon$ and $r_m$ parameters in good agreement with the experimental values for all Kr–Ng systems.$^{27,36}$ This confirms that the Kr–Ng systems are all prototypical van der Waals complexes whose interaction is exclusively due to the balance between size repulsion and long range...
dispersion attraction. This interaction, in all the asymmetrical Ng–Ng′ systems, does cause, of course, a more or less pronounced polarization of the electron clouds (see, e.g., Fig. 2 of Ref. 13) and the consequent emergence of a dipole moment (see, e.g., Ref. 39). But it does not give rise to appreciable charge transfer. Since polarizability of Kr is slightly larger than that of NH₃, we assume that the Kr–Ng interactions must represent an upper limit of the van der Waals component for the homologous NH₃–Ng aggregates. As expected, correlation formulas predict for NH₃–Ng aggregates potential parameters which are, in general, slightly (but significantly) lower with respect to the corresponding ones of Kr–Ng (see Table I). Therefore, this analysis suggests that a direct comparison of the experimental cross sections for Kr and ammonia scattered by the same target may be attempted in order to obtain an insights into the nature of the involved interaction.

Figures 5 and 6 show cross sections $Q(v)$ for all NH₃–Ng complexes, calculated by using the present potentials (see Table I and Fig. 3). In Fig. 6 the data are plotted as $Q(v)v^{2/5}$ for a better evaluation of the positions of the glory extrema. In the same figures are also reported, for each case, results of calculations carried out with the accurately characterized interaction potentials of the corresponding Kr–Ng system (see Table I). The attention should be focused both on the absolute...
The figure shows that while the C\textsubscript{6}–Ng systems (range attraction coefficient (C\textsubscript{6})) of the NH\textsubscript{3}–Ng to that of the corresponding Kr–Ng systems (r\textsubscript{0} and C\textsubscript{6}) plotted as a function of the polarizability of Ng (in Å\textsuperscript{3}). Dashed lines have been drawn at the reference ratio of 0.90 (see text).

value of the cross section and on the position of the glory extrema.

For all NH\textsubscript{3}–Ng complexes the average cross sections appear to be systematically smaller with respect to the corresponding ones of Kr–Ng and this deviation arises from a lower attraction (dispersion + induction) at long range (see the values of the C\textsubscript{6} coefficients in Table II). This behavior is also in agreement with the expectation from the lower value of the ammonia polarizability with respect to that of Kr. For NH\textsubscript{3}–He and NH\textsubscript{3}–Ne also the depth of the potential well appears to be less deeper with respect to that of the corresponding Kr–He and Kr–Ne systems, as further evidenced, for NH\textsubscript{3}–Ne, by the relative position of the glory extremum, clearly shifted at lower velocity (see Fig. 6). Interestingly, such shift becomes less evident for NH\textsubscript{3}–Ar, while the glory extrema of NH\textsubscript{3}–Kr and Kr–Kr are nearly coincident. For the NH\textsubscript{3}–Xe case a shift at higher velocities is observed. This finding suggests that an additional interaction component, ineffective at long range, emerges at intermediate and short intermolecular distances and produces a deepening of the potential well, whose amount increases along the Ng family. For NH\textsubscript{3}–Kr the nearly zero shift of the glory extrema with respect to Kr–Kr indicates a balance between a lower attraction and the intermolecular bond stabilization due to such additional interaction component.

We can also put this phenomenology more clearly in evidence, by plotting in Fig. 7 well depth and long range coefficients ratios, for the corresponding NH\textsubscript{3}–Ng and Kr–Ng systems, as a function of the Ng polarizability (with exclusion of NH\textsubscript{3}–He for which no glory pattern has been observed). The figure shows that while the C\textsubscript{6} ratio is practically constant along the Ng series, confirming that the long range attraction scales consistently for all systems, the well depth ratio increases regularly in going from Ne to Xe. Assuming that the combination of van der Waals plus induction components provides a well depth ratio equal to 0.90 for all systems (as suggested by NH\textsubscript{3}–Ne and confirmed by the average C\textsubscript{6} ratio) we can obtain in absolute scale the value of such additional component (see Table III) which is not measurable (it is below the experimental sensitivity) for NH\textsubscript{3}–Ne and increases along the Ng family up to 15% of the full interaction for the NH\textsubscript{3}–Xe system. Finally, note that results in Table III are also consistent with the differences among experimental and predicted depth of the potential wells (see Table II).

V. CONCLUSIONS

The present paper reports on the characterization of the average intermolecular interaction in the ammonia–noble gas complexes, based on integral scattering cross section measurements in a wide collision velocity range and with an experimental resolution sufficient to resolve for all cases (except for NH\textsubscript{3}–He) the glory quantum interference pattern. The data analysis and the comparison with similar systems investigated with the same methodology permitted us to reveal the presence, and to evaluate the strength, of an interaction component which adds to the van der Waals plus induction interaction. This interaction component provides for the ammonia–heavier noble gas systems an evident intermolecular bond stabilization. This behavior is similar to that recently characterized for the water–noble gas complexes\textsuperscript{5,9,13} and therefore, in analogy with the latter, we suggest that such additional interaction component may arise from charge (electron) transfer effects. Such effects, related to the overlap between electron clouds and therefore vanishing at long range, depend on the nature of the ammonia interacting partners and on the ammonia orientation. Under the present experimental conditions (rotational hot molecules) the cross sections are expected to be affected by the spherically averaged amount of charge transfer at intermolecular distances around r\textsubscript{m}. The effect will manifest itself as a glory shift in the cross section due to the related deepening of the radial potential well. This hypothesis has been confirmed\textsuperscript{40} by an \textit{ab initio} analysis of the electron density displacements, associated with the intermolecular complex formation, where dependencies on the noble gas atom and on the ammonia molecule orientation have also been investigated. By coupling experimental and theoretical information we hope to obtain further insight on the relation between charge (electron) transfer and bond stabilization, including its stereospecificity and radial dependence. In conclusion, the study of an ample

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<th>System</th>
<th>Bond stabilization (meV)</th>
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<tbody>
<tr>
<td>NH\textsubscript{3}–Ne</td>
<td>0 ± 0.3</td>
</tr>
<tr>
<td>NH\textsubscript{3}–Ar</td>
<td>0.7 ± 0.7</td>
</tr>
<tr>
<td>NH\textsubscript{3}–Kr</td>
<td>2.1 ± 0.9</td>
</tr>
<tr>
<td>NH\textsubscript{3}–Xe</td>
<td>3.6 ± 1.0</td>
</tr>
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</table>

TABLE III. Additional interaction component (bond stabilization energy) (meV) in the neighborhood of the equilibrium distance (see the text).
phenomenology of weakly bound systems, involving hydrogenated molecules and closed electronic shell partners, could be crucial to achieve this target under conditions where charge transfer provides only perturbative effects (see for instance Ref. 41).

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