Theoretical and REMPI spectroscopic study on phenylhydrazine and phenylhydrazine–(Ar)$_n$ ($n = 1, 2$) van der Waals complexes

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Phenylhydrazine and its van der Waals complexes with one or two argon atoms were investigated with theoretical calculations and resonant two photon ionization (R2PI) spectroscopy. The \textit{ab initio} and DFT calculations found a conversion of the orbital hybridization of the N$_n$ atom from sp$^3$-like in the S$_0$ state to sp$^2$-like in the S$_1$ state, suggesting that the lone pair electrons of the N$_n$ atom are involved in a super p–p–π conjugation over the skeleton of phenylhydrazine in the S$_1$ state. The structural change of the hydrazino group in the S$_1$ ← S$_0$ electronic transition was reflected by the vibrational excitations of the hydrazino group observed in the 1C-R2PI spectrum. The band origin of the S$_1$ ← S$_0$ transition is determined to be 33610 cm$^{-1}$ and the adiabatic ionization energy (IE) of phenylhydrazine, measured by 2C-R2PI spectroscopy, is 62829 ± 15 cm$^{-1}$. The S$_1$ ← S$_0$ electronic transitions of phenylhydrazine–Ar and phenylhydrazine–Ar$_2$ complexes were also observed in the 1C-R2PI spectrum, and their band origins are, respectively, red-shifted by 39 and 80 cm$^{-1}$ from that of phenylhydrazine.

1. Introduction

Phenylhydrazine is famous as a reagent in the determination and separation of simple sugars from their natural mixture. Also, it is widely used as an intermediate for manufacture of pharmaceuticals, pesticides and dyestuffs. However, phenylhydrazine and its derivatives have been regarded as suspected carcinogens and are harmful to aquatic life. Because of their high toxicity and poor biodegradability, the efficient determination and removal of them from waste streams has become a significant environmental concern. Study on the molecular properties in different electronic states will be helpful in understanding the general chemistry of phenylhydrazine. Phenylhydrazine can be regarded as a benzene derivative or an N-amino substituted aniline. Previous studies have been focused on N-alkyl anilines. Their neutral molecules in the ground S$_0$ and electronically excited S$_1$ states, as well as the cations in ground D$_0$ state, were extensively investigated, which have lead us to a better understanding about the effect of N-alkyl substitution on the molecular properties including structure, electronic transition energy and molecular vibration. Compared to the alkyl group, the amino group has a higher electronegativity and hence usually shows an electron-withdrawing inductive effect in organic compounds, while the lone pair electrons of the nitrogen atom are capable of forming the p–π conjugation with the neighboring π bond, which gives an electron donating effect. The N-amino substitution on aniline may result in new photochemical processes or photo-physical phenomena, since the nature and location of the substituents in benzene derivatives bring about discrete molecular properties as well as chemical reactivity.

Combined with theoretical calculations, resonance-enhanced two-photon ionization (R2PI) spectroscopy has been used successfully to probe the photophysical and photochemical properties of aromatic molecules, complexes and clusters. Since the R2PI process occurs when the laser wavelength is tuned to a real intermediate state of the molecule, it can be used to select a particular species from a mixture which is referred as the fingerprint for molecular identification. To the best of our knowledge, the optimized geometries and vibrations of phenylhydrazine in the electronically excited S$_1$ state are still not available in the literature. The theoretical and R2PI spectroscopic study on phenylhydrazine can provide not only useful information of molecular properties, but also a promising method for the determination of phenylhydrazine.

Molecular clusters can serve as a bridge between the gaseous and condensed phases, enabling interesting aspects of the condensed phase to be studied at the molecular level. Weakly bound van der Waals (vdW) complexes of aromatic molecules with rare gas atoms have been extensively investigated in the past few decades. The vdW complexes of aniline with argon atoms have been especially intensively studied, but a similar study on the vdW complexes of phenylhydrazine with argon atoms is still lacking.

In this paper, we report the results of the theoretical and R2PI spectroscopic study on phenylhydrazine in the excited S$_1$ state, including its molecular structure and vibrations, the S$_1$ ← S$_0$ electronic transition energy and the adiabatic ionization energy (IE) measured by two-color resonant two-photon ionization (2C-R2PI) spectroscopy. The S$_1$ ← S$_0$ electronic transition band origins ($E_{00}$) of phenylhydrazine–Ar and phenylhydrazine–Ar$_2$ vdW complexes, as well as their optimized structures based on MP2 calculations, are also presented.
2. Experimental and computational methods

The experimental apparatus is essentially similar to that used in previous studies. The supersonic free-jet expansion was generated by a pulsed valve (General Valve) with an orifice diameter of 0.25 mm. The stagnation pressure was 3 atm or 5 atm for the studies of phenylhydrazine and its vdW complexes, respectively. Phenylhydrazine (Aldrich, 98%) was used without further purification. The sample was heated to about 450 K to get sufficient vapor pressure. In the ionization chamber, the ionization of phenylhydrazine was generated at 70 mm from the nozzle orifice by a UV laser beam perpendicular to the molecular beam. The ions were mass-analyzed by a time-offlight mass spectrometer with a 1.0-meter long flight tube.

The UV laser was produced by doubling the frequency of two dye lasers (Sirah Dye Laser-CSTR and PDL-3) pumped by the second harmonic or the third harmonic of an Nd:YAG laser (Quanta-Ray, PRO-Series, pulse width, 8–10 ns) at a repetition rate of 10 Hz. The synchronization of the YAG laser with the pulsed valve was controlled by a pulse-delay generator (DG535, Stanford Research System). The frequency of the UV laser was calibrated with the REMPI frequencies of I (2P3/2) and P (3P1/2) of methyl iodide. The deviation of the frequency calibration was below 0.15 cm⁻¹. In the 2C-R2PI experiment, the spatial widths of the excitation and ionization UV laser beams were held at about 1 mm and 3 mm in the interaction zone, respectively. The wavelength of the excitation laser was fixed to the strongest transition to a particular vibration in the S₁ state, and that of the ionization laser was scanned around the adiabatic ionization energy of phenylhydrazine. The excitation and ionization laser powers were adjusted in such a way that the ratio of the 2C-R2PI signals to 1C-R2PI signals was about 30:1.

The ion signals were amplified by a preamplifier (SR445A, Stanford Research System) and then collected and analyzed by a multi-channel scaler (MCS, Stanford Research System, SR430). Both of the Sirah Dye Laser and the MCS were controlled by a personal computer. The time-gated mass spectra were accumulated for 200 laser shots for each wavelength. The wavelength was scanned at 1.2 cm⁻¹ spacing.

Ab initio and density functional theory (DFT) calculations were performed with the Gaussian 03W program package. The labeling of the carbon atoms is 1–6 around the ring and the substituted portions are labeled as C₁–Nₓ–Nᵧ; the C₂ atom is close to the terminated amino group. The restricted B3LYP/6-311 + + (d, p) and MPW1PW91/6-311 + + (2df, 2pd) were applied to calculations of the ground state (S₀), while the CIS/6-311 + + (d, p) and the CIS/6-311 + + (2df, 2pd) methods were applied to calculations of the excited state (S₁). The MP2/6-311 + + (d, p) method with zero-point energy (ZPE) corrections was used to calculate the equilibrium structures of the vdW complexes.

3. Results and discussion

3.1 Optimized molecular structures of phenylhydrazine in the S₀ and S₁ states

The optimized equilibrium structure of phenylhydrazine in the excited S₁ state is quite different from that in the ground S₀ state, especially at the hydrazino group (as shown in Fig. 1). The optimized structures of hydrazine in the ground S₀ state and the excited S₁ state are also shown in Fig. 1. The C₂ symmetry of hydrazine in the S₀ state is consistent with the results of previous studies with ab initio calculations and experiments, and is similar to that of the hydrazino group of phenylhydrazine in the S₀ state. The planar structure of hydrazine in the S₁ state is also similar to that of the hydrazino group of phenylhydrazine in the S₁ state, though one of the H₈ atoms is slightly bent out of the ring plane in phenylhydrazine. This seems that, just like in hydrazine, the S₁ ← S₀ electronic transition of phenylhydrazine is mainly related to the transition of a nonbonding electron of a nitrogen atom to an antibonding σ* orbital. However, it has been reported that the S₁ ← S₀ electronic transition of benzene and substituted benzenes is mainly subject to the π* ← π transition of the aromatic ring. It would be interesting to find out why the π* ← π transition of the aromatic ring can induce the significant structural change of the hydrazino group. For aniline, the p–π conjugation is enhanced in the S₁ state and hence causes the amino group to be planar. For phenylhydrazine in the S₁ state, it’s reasonable that the p–π conjugation may also be enhanced: while the terminated amino group is not directly connected to the aromatic ring, it seems that it should maintain the pyramidal structure. However, the calculations predict that the terminated amino group is almost planar, implying that it might be involved in conjugation with the aromatic ring.

The parameters of the optimized structure of phenylhydrazine in the S₀ and S₁ states are listed in Table 1. For the S₀ state, the structural parameters calculated at the B3LYP/6-311 + + (d, p) level are very close to those calculated at the
MPW1PW91/6-311+++(df, 2pd) level, while for the S1 state, the structural parameters calculated at the CIS/6-311+++(d, p) level are very close to that calculated at the CIS/6-311+++(2df, 2pd) level. These suggest that the equilibrium structures of phenylhydrazine in the S0 and S1 states were well-optimized by the calculations. In the following discussion, the parameters achieved with the MPW1PW91/6-311+++(df, 2pd) level and the CIS/6-311+++(2df, 2pd) level will be used to compare the equilibrium structures of the two states. Upon the S1 ← S0 electronic transition, the C–N bond becomes shorter, exhibiting more double bond character in the S1 state than in the S0 state. It might be caused by the stronger p–π conjugation in the S1 state. This kind of phenomena were also observed in p-fluoroaniline47 and styrene derivatives26,48,49 etc., in which the C–N bond and C1–C2 bond become shorter in the S1 ← S0 electronic transition. Notably, the N–N bond of phenylhydrazine is remarkably shortened from 1.394 Å in the S0 state to 1.314 Å in the excited S1 state. Since the typical N–N and N=C=N bond lengths in hydrazine and azomethane are respectively 1.449 and 1.247 Å,30 the decrease of the N–N bond length means that this bond in the excited S1 state exhibits a partial double bond character. Contrarily, the C=C double bond in styrene derivatives26,48,49 is lengthened in the S1 ← S0 electronic transition.

Upon the S1 ← S0 electronic transition of phenylhydrazine, the Hβ–Nβ–Hα angle is increased from 109.7° to 115.7° (the H–C–H angle in ethylene is only 116.7°), which indicates that the orbital hybridization of the Nβ atom may experience a conversion from sp2-like in the S0 state to sp3-like in the S1 state. This is confirmed by the increase of the two Hβ–Nβ–Nα angles, from 112.3° and 109.8° to 115.9° and 113.3° upon the S1 ← S0 transition. Both the partial double bond Nα–Nβ and the sp2-like orbital hybridization of the Nβ atom suggest that the lone pair electrons of the Nβ atom are involved in a super p–p–π conjugation over the skeleton of phenylhydrazine in the S1 state (as shown in Fig. 1c). The p–π conjugation between the Nα atom and the benzene ring is common, which occurs in the S0 state but is enhanced in the S1 state, just as in aniline. Probably the two half-occupied orbitals (π and π*) produced in the S1 ← S0 transition can enhance the p–π conjugation of phenylhydrazine in the S1 state and consequently cause the formation of the super p–p–π conjugation. The super p–p–π conjugation is different from the π–π conjugations in styrene: four π-electrons of the two nitrogen atoms are delocalized in the former, while only two π-electrons of the vinyl group are delocalized in the latter.

For phenylhydrazine in the S0 state, the H3 and Nβ atoms are on the same side of the aromatic ring plane and bent out of the ring plane by 22.3° and 19.4°, respectively; however, when excited to the S1 state, the H3 and Nβ atoms are on opposite sides of the aromatic ring plane and bent out of the ring plane only by 7.9° and 2.0°, respectively. The dihedral angle Nβ–Nα–C1–C2 is only 2.0°: the skeleton of phenylhydrazine in the S1 state is almost planar.

The symmetry of phenylhydrazine molecular structure belongs to the C1 point group in both the S0 and S1 states, while the corresponding symmetry of aniline belong to Cs and C2v point groups in the S0 and S1 states, respectively. The ground S0 state of aniline has a non-planar structure with the hydrogen atoms of the amino group bent out of the aromatic plane by about 42°.51 When aniline is excited to the S1 state, the bending angle vanishes as the hydrogen atoms move to the plane of the aromatic ring.46 A similar structural change was also found in the S1 ← S0 electronic transition of p-fluoroaniline.52,53 Tzeng et al. have successfully predicted the optimized geometry of p-fluoroaniline in the S1 state by CIS/6-31+G* calculation.47 The delocalization of the lone paired electrons of the amino group to the aromatic ring causes the aniline and p-fluoroaniline in the S1 state to have a planar structure. In the molecular structure of phenylhydrazine in the S1 state (Fig. 1c), the distance between the Hβ atom and the nearby hydrogen atom of the aromatic ring is only 2.28 Å, shorter than double the van der Waals radius of hydrogen. This suggests that the steric effect between the

Table 1  The calculated bond lengths (Å) and bond angles (°) of phenylhydrazine in the S0 and S1 states.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S0</th>
<th>MPW1PW91/6-311+++(df, 2pd)</th>
<th>S1</th>
<th>CIS/6-311+++(d, p)</th>
<th>CIS/6-311+++(2df,2pd)</th>
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<tr>
<td>Nα–Nβ</td>
<td>1.410</td>
<td>1.394</td>
<td>1.318</td>
<td>1.314</td>
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<tr>
<td>Nα–C1</td>
<td>1.404</td>
<td>1.392</td>
<td>1.352</td>
<td>1.347</td>
<td></td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.401</td>
<td>1.393</td>
<td>1.405</td>
<td>1.402</td>
<td></td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.393</td>
<td>1.386</td>
<td>1.374</td>
<td>1.370</td>
<td></td>
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<tr>
<td>C3–C4</td>
<td>1.393</td>
<td>1.386</td>
<td>1.393</td>
<td>1.390</td>
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</tr>
<tr>
<td>C4–C5</td>
<td>1.395</td>
<td>1.388</td>
<td>1.387</td>
<td>1.384</td>
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<tr>
<td>C5–C6</td>
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<td>1.383</td>
<td>1.397</td>
<td>1.392</td>
<td></td>
</tr>
<tr>
<td>C6–C1</td>
<td>1.404</td>
<td>1.397</td>
<td>1.405</td>
<td>1.402</td>
<td></td>
</tr>
<tr>
<td>(\angle HβNβHα)</td>
<td>109.8</td>
<td>109.7</td>
<td>115.4</td>
<td>115.7</td>
<td></td>
</tr>
<tr>
<td>(\angle NαNβC1)</td>
<td>117.6</td>
<td>118.0</td>
<td>126.4</td>
<td>126.7</td>
<td></td>
</tr>
<tr>
<td>(\angle NαC1C2)</td>
<td>122.1</td>
<td>122.1</td>
<td>122.8</td>
<td>122.8</td>
<td></td>
</tr>
<tr>
<td>(\angle NαC2C3)</td>
<td>118.8</td>
<td>119.0</td>
<td>117.1</td>
<td>117.1</td>
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<tr>
<td>(\angle NαC3C4)</td>
<td>120.4</td>
<td>120.5</td>
<td>120.1</td>
<td>120.1</td>
<td></td>
</tr>
<tr>
<td>(\angle C3C4C5)</td>
<td>120.6</td>
<td>120.6</td>
<td>120.3</td>
<td>120.3</td>
<td></td>
</tr>
<tr>
<td>(\angle C4C5C6)</td>
<td>118.9</td>
<td>118.8</td>
<td>120.1</td>
<td>120.1</td>
<td></td>
</tr>
<tr>
<td>(\angle C5C6C1)</td>
<td>121.2</td>
<td>121.2</td>
<td>120.6</td>
<td>120.7</td>
<td></td>
</tr>
<tr>
<td>(\angle C6C1C2)</td>
<td>119.9</td>
<td>119.9</td>
<td>119.2</td>
<td>119.2</td>
<td></td>
</tr>
<tr>
<td>(\angle NαNαC1C2)</td>
<td>–20.8</td>
<td>–19.4</td>
<td>2.7</td>
<td>2.0</td>
<td></td>
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<tr>
<td>(\angle HαNαC1C2)</td>
<td>23.0</td>
<td>22.3</td>
<td>9.5</td>
<td>7.9</td>
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terminated amino group and the nearby hydrogen atom of the ring may cause the hydrazino group to be distorted out of the aromatic plane, although the formation of the p–p–π conjugation requires a planar structure in the S1 state. In fact, the dihedral angle N–N–C1–C2 is decreased from 19.4° in the S0 state to 2.0° in the S1 state. The N–N–C1 angle in the S1 state is increased by 8.7° with respect to that of the ground S0 state, which may also be caused by the steric effect.

Since the S1 ← S0 electronic transition of benzene and substituted benzenes is mainly subject to the π* ← π transition of the aromatic ring, usually the aromatic ring expands in the S1 ← S0 transition. However, the benzene ring of phenylhydrazine slightly shrinks in the S1 ← S0 transition. This might be due to the delocalization of the lone pair electrons of the nitrogen atoms to the π bonding orbital of benzene ring, which consequently enhances the bonding effect of the benzene ring. It supports the formation of the super p–p–π conjugation over the skeleton of phenylhydrazine in the excited S1 state. The present calculations indicate that the S1 ← S0 transition of phenylhydrazine brings a significant change in molecular structure, which has been indirectly reflected in the R2PI spectrum.

### 3.2 R2PI spectrum of phenylhydrazine

The 1C-R2PI spectrum of phenylhydrazine is shown in Fig. 2a. The peaks denoted by the asterisk correspond to the band origins of phenylhydrazine–Ar and phenylhydrazine–Ar2 vdW complexes, which will be discussed later. The observed vibrational frequencies of phenylhydrazine in the excited S1 state in Fig. 2a are summarized in Table 2, along with the calculated frequencies and assignments. The phenylhydrazine molecule has 42 vibrational modes including 30 benzene-like modes and 12 hydrazino group modes. Since the intensity of each vibronic band is related to the Franck-Condon overlaps, not all transitions with different vibrational excitation can be observed in the present R2PI spectrum. The assignments of the experimental spectral bands are mainly based on ab initio calculations and the conformity with the vibrations of aniline and N-alkyl anilines in the excited S1 state. The vibrational modes are expressed in the Varsanyi and Szoke's notation based on benzene vibrational modes. When the calculated frequencies are scaled by 0.91, the predicted normal-mode frequencies match well to the measured ones.

The intense band at the one-photon energy of 33610 cm⁻¹ is identified as the band origin (0°) of the S1 ← S0 electronic transition of phenylhydrazine. The CIS/6-311++G(d,p) calculation predicts the electronic transition energy to be 32554 cm⁻¹, about 3.1% lower than the measured one, while the CIS/6-311++G(2df,2pd) calculation predicts the electronic transition energy to be 32411 cm⁻¹, about 3.6% lower than the measured one. The band origin of phenylhydrazine is red-shifted by 419 cm⁻¹ with respect to that of aniline, while the band origin of N-methylaniline is red-shifted by 737 cm⁻¹ with respect to that of aniline. It is interesting to note that, though the amino group and the methyl group have different inductive effects, their π-substitution on aniline give a similar effect on the S1 ← S0 electronic transition energy: both cause the transition energy to be red-shifted. It seems that the

![Fig. 2](image_url) (a) 1C-R2PI spectrum of phenylhydrazine in the excited S1 state (peaks denoted by an asterisk correspond to the band origins of phenylhydrazine–Ar and phenylhydrazine–Ar2 vdW complexes). (b) The 2C-R2PI spectrum of phenylhydrazine by ionization via S1 6a1 state.

<table>
<thead>
<tr>
<th>Observed bands (cm⁻¹) and assignment of the R2PI spectrum of phenylhydrazine</th>
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<tbody>
<tr>
<td>Exp.</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>33610</td>
</tr>
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<td>33755</td>
</tr>
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<td>33799</td>
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<tr>
<td>34829</td>
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<td>34988</td>
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</tbody>
</table>

*Obtained from CIS/6-311++G(2df,2pd) calculations (scaled by 0.91).

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formation of the super p–p–π conjugation over the skeleton of phenylhydrazine in the excited S1 state can make the terminated amino group an electron donor. Since the S1 ↔ S0 electronic transition of benzene and substituted benzenes is mainly subject to the π* ↔ π transition of the aromatic ring, for aniline, the amino group shares its lone pair electrons over the ring by p–π conjugation which leads to a larger change of the electron density distribution on the ring, following by a decrease of the zero point level (ZPL) energy when excited to the S1 state. So the nature of the substituent on the amino group will indirectly influence the electron density of the aromatic ring. The red-shift of the electronic transition energy of N-methylaniline with respect to that of aniline is 318 cm\(^{-1}\) larger than that of phenylhydrazine, which may originate mainly from their different inductive effects in the S0 state.

In the 1C-R2PI spectrum, the bands with frequencies higher than that of the band origin are related to the active vibrations of phenylhydrazine in the excited S1 state. Most of the vibronic bands have been tentatively assigned to the fundamental normal vibrations of benzene ring and hydrazino group in the excited S1 state. The band located at 768 cm\(^{-1}\) is assigned to the in plane ring deformation mode 1\(_b\), which is usually referred to the breathing motion. The most intense band at 420 cm\(^{-1}\) is assigned to the transition mode 6a\(_b\), which involves the in plane ring deformation. It is known that most of the normal mode vibrations of the aromatic ring in substituted benzenes are quite similar to those of benzene.\(^{58}\)

However, the normal vibrational modes involving motions of the ring carbon-atoms at the substitution position depend upon the nature of the substituted group and the pattern of the vibration. For example, the respective vibrational frequencies of mode 6a in the excited S1 state are 492, 441 and 420 cm\(^{-1}\) for aniline,\(^{56}\) N-methylaniline\(^6\) and phenylhydrazine, while the frequencies of the mode 1\(_b\) in the excited S1 state for aniline,\(^{56}\) N-methylaniline\(^6\) and phenylhydrazine are 797, 775 and 768 cm\(^{-1}\), respectively. Both the N-methyl substitution and the N-amino substitution cause the frequencies of the two vibrations to decrease with respect to that of benzene. The nature of the substituent is responsible for the deviation in the vibrational frequencies. Usually, the methyl group and the amino group are referred to as the electron-donating and electron-withdrawing substituents, respectively, but here the N-amino group seems to have an electron-donating effect. This can also be explained by the formation of the super p–p–π conjugation over the skeleton of phenylhydrazine in the excited S1 state.

The bands at 380, 481 and 686 cm\(^{-1}\) are assigned to the out-of-plane skeletal vibrations of 16a\(_b\), 16b\(_b\) and 4b\(_b\), respectively. The band at 912 cm\(^{-1}\) is related to the C–H out-of-plane bending vibrational mode 17b\(_b\), and those bands at 1219 and 1378 cm\(^{-1}\) are assigned to the C–H in plane bending vibrational modes 9b\(_b\) and 3b\(_b\), respectively. The bands at 145, 189, 715 and 1181 cm\(^{-1}\) are determined to be related to the vibrations of the hydrazino group. The weak band observed at 145 cm\(^{-1}\) is assigned to the out-of-plane bending vibration of the terminated amino group, while the band at 189 cm\(^{-1}\) is assigned to the torsion vibration of the hydrazino group. The moderately intense band at 715 cm\(^{-1}\) is tentatively assigned as the hydrazino inversion motion, in which all the three N–H bonds experience bending. This kind of inversion motion seems to be triggered easily in the structural transition of hydrazino group from the gauche structure in the S0 state to a near-planar structure in the S1 state. Similarly, the amino inversion motion with a frequency of 760 cm\(^{-1}\) has been observed in the S1 ↔ S0 electronic transition of aniline.\(^{56}\) The band at 1181 cm\(^{-1}\) is related to the stretching vibration of C–N\(_a\) and N\(_a–N_b\) bonds.

Combination bands of in-plane and out-of-plane fundamental vibrations are also evident in the 1C-R2PI spectrum. The three weak bands at 673, 873 and 1137 cm\(^{-1}\) are assigned as the combination bands formed between the hydrazino group vibrations and the ring vibrations, as seen in Table 2. These assignments are based on ab initio calculations and the comparison of the observed frequencies and intensities with those of the corresponding transitions in the R2PI spectrum. Among the 15 vibrational bands observed, there are 7 bands associated with the vibrational excitations of the hydrazino group. This may reflect the significant structural change of the hydrazino group in the S1 ↔ S0 electronic transition.

The adiabatic ionization energy (IE) of phenylhydrazine was measured with two color resonant two photon ionization (2C-R2PI) spectroscopy on the present experimental setup. Fig. 2b shows the 2C-R2PI spectrum of phenylhydrazine recorded by ionization via resonant excitation to the most-pronounced band of 6a\(_b\) vibration in the excited S1 state. In consideration of the uncertainty in the laser photon energy and Stark effect, the adiabatic IE of this molecule is determined to be 62829 ± 15 cm\(^{-1}\) (7.7898 ± 0.0019 eV), which is in accordance with the reported values in the literature ranging from 7.64 eV to 7.86 eV.\(^{59}\)

### 3.3 Phenylhydrazine–Ar and phenylhydrazine–Ar2 van der Waals complexes

The phenylhydrazine–Ar\(_p\) (p = 1–4) van der Waals complexes were observed in the TOF mass spectrum under a backing pressure of 5.0 atm, as shown in Fig. 3a. It is well known that the red shift of the S1 ↔ S0 electronic transition for the vdW complex containing two rare gas atoms with respect to the band-origin of the bare molecule is very close to twice the shift for the vdW complex containing one rare gas atom. The bands labeled with the asterisk in Fig. 2a are red-shifted by approximately 39 and 80 cm\(^{-1}\) from the band-origin of phenylhydrazine, and their intensity can be improved by increasing the stagnation pressure (Fig. 3b), suggesting they are not the hot bands. Hence the two bands are tentatively assigned to the phenylhydrazine–Ar and phenylhydrazine–Ar2 van der Waals complexes. No band in the 1C-R2PI spectrum can be assigned to PH–Ar3 and PH–Ar4 van der Waals complexes. Knee et al.\(^{16}\) have studied the binding energies and dissociation pathways of aniline–Ar and aniline–Ar2 cations. The binding energies of [aniline–Ar]\(^+\) and [aniline–Ar2]\(^+\) are determined to be 495 ± 15 cm\(^{-1}\) and 1020 ± 15 cm\(^{-1}\), respectively. Suppose that [phenylhydrazine–Ar]\(^+\) and [phenylhydrazine–Ar2]\(^+\) have similar binding energies as much as that of [aniline–Ar]\(^+\) and [aniline–Ar2]\(^+\), respectively. The two-photon energy in the 1C-R2PI process of a complex is estimated to be larger than the ionization energy of the complex by about 4000 cm\(^{-1}\). Since the excess energy is much larger than the binding energy...
of the complex cation, it may dissociate when the neutral complexes are ionized. So, it is reasonable that the spectral signals of the complexes can be achieved in the time-gate of phenylhydrazine in the TOF-MS. Similar phenomenon has been observed in the 1C-R2PI spectrum of $p$-dimethoxybenzene–Ar$_n$ complexes.

We have conducted calculations to predict the geometries of phenylhydrazine–Ar and phenylhydrazine–Ar$_2$ complexes using MP2/6-311++(d, p) calculations. A number of starting configurations were chosen in order to find possible multiple minima on the complexes potential energy surface, and the frequency calculations are employed to determine the zero-point energy (ZPE) contribution to the binding energy. The optimized stable structures of the complexes in the ground state are shown in Fig. 4. Since the terminated amino group is located out of the aromatic ring, there exist two stable isomers of phenylhydrazine–Ar complex. The “up” isomer is named for the argon atom located at the same side of the aromatic ring as the amino group, and the “down” isomer is named for the argon atom located at the other side. The binding energies of the “up” and “down” isomers are calculated to be 943.7 and 823.7 cm$^{-1}$, respectively. The calculations indicate that the “up” isomer is only 120 cm$^{-1}$ more stable than the “down” isomer. For a complex containing two rare gas atoms, it seems that the second rare-gas atom is situated at a symmetric position on the other side of the aromatic ring. Similarly, the calculations on the phenylhydrazine–Ar$_2$ complex predicted the most stable configuration with the argon atoms occupying almost symmetrical positions on the opposite sides of the aromatic ring, as shown in Fig. 4. Relative C$_1$–Ar positions in phenylhydrazine–Ar$_2$ complex are similar to those in phenylhydrazine–Ar isomers. The binding energy of phenylhydrazine–Ar$_2$ complex is calculated to be 1755.3 cm$^{-1}$, slightly lower than the sum of the binding energies of the two different phenylhydrazine–Ar configurations.

4. Conclusion

The $ab$ initio and DFT calculations have been applied to predict the molecular structure of phenylhydrazine in the ground $S_0$ state and the excited $S_1$ state, which found a significant change of structure in the $S_1 \leftrightarrow S_0$ electronic transition. For phenylhydrazine in the $S_0$ state, the hydrazino group is present as a gauche conformer, while in the $S_1$ state, the hydrazino group is almost planar. Upon the $S_1 \leftrightarrow S_0$ electronic transition the lone pair p-electrons of the nitrogen atoms are involved in a super p–p–p conjugation over the skeleton of phenylhydrazine in the $S_1$ state. This kind of p–p–p conjugation is different from the p–p conjugation in styrene, because the two nitrogen atoms of the hydrazino group provide 4 p-electrons to the p–p–p conjugation, while the two carbon atoms in the vinyl group provide only 2 π-electrons to the p–π conjugation.

The vibrationally resolved spectrum of phenylhydrazine in the excited $S_1$ state was achieved for the first time. The observed spectral features show that most of the active vibronic transitions are related to the benzene ring normal vibrations and the hydrazino group normal vibrations in the excited $S_1$ state. The significant structural change of the hydrazino group in the $S_1 \leftrightarrow S_0$ electronic transition was reflected by the vibrational excitations of the hydrazino group observed in the 1C-R2PI spectrum. The $S_1 \leftrightarrow S_0$ electronic transition energy is determined to be 33610 cm$^{-1}$, and the adiabatic ionization energy (IE) measured by two 2C-R2PI spectroscopy is 62829 ± 15 cm$^{-1}$. The measured IE is more precise than the previously accepted value ranging from 7.64 to 7.86 eV measured by photoelectron spectroscopy.

The phenylhydrazine–Ar$_n$ ($n = 1–4$) van der Waals complexes were observed in the TOF mass spectrum. The band origins of phenylhydrazine–Ar and phenylhydrazine–Ar$_2$ vdW complexes are found to be red-shifted by 39 and 80 cm$^{-1}$ with...
respect to that of phenylhydrazine. The calculations indicate that the relative C1–Ar positions in the phenylhydrazine–Ar2 complex are much the same as that in phenylhydrazine–Ar isomers. The binding energy of phenylhydrazine–Ar2 complex is slightly lower than the sum of the binding energies of the two different phenylhydrazine–Ar configurations.

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