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With infrared absorption spectra we investigated the reaction between Cl atom and pyridine (C₅H₅N) in a para-hydrogen (p-H₂) matrix. Pyridine and Cl₂ were co-deposited with p-H₂ at 3.2 K; a planar C₅H₅N–Cl₂ complex was identified from the observed infrared spectrum of the Cl₂/C₅H₅N/p-H₂ matrix. Upon irradiation at 365 nm to generate Cl atom in situ and annealing at 5.1 K for 3 min to induce secondary reaction, the 1-chloropyridinyl radical (C₅H₅N–Cl) was identified as the major product of the reaction Cl + C₅H₅N in solid p-H₂; absorption lines at 3075.9, 1449.7, 1200.6, 1148.8, 1069.3, 1017.4, 742.9, and 688.7 cm⁻¹ were observed. The assignments are based on comparison of observed vibrational wavenumbers and relative IR intensities with those predicted using the B3PW91/6-311++G(2d, 2p) method. The observation of the preferential addition of Cl to the N-site of pyridine to form C₅H₅N–Cl radical but not 2-, 3-, or 4-chloropyridine (ClC₅H₅N) radicals is consistent with the reported theoretical prediction that formation of the former proceeds via a barrierless path. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789407]

I. INTRODUCTION

The reaction of atomic chlorine (Cl) with pyridine (C₅H₅N) has drawn much attention in atmospheric chemistry because pyridine is emitted into the atmosphere as a result of industrial activities such as the production of insecticides and herbicides and the combustion of coal; Cl atoms might have concentrations large enough to oxidize atmospheric pollutants in the marine and coastal atmosphere.¹–³ This reaction is important also in organic chemistry because the selectivity of tertiary versus primary hydrogen abstraction in photochlorination reactions is enhanced significantly when the reactions are conducted in solvents such as benzene and pyridine; the selectivity is attributed to formation of weakly bound complexes between Cl and benzene or pyridine.⁴⁻⁵ The use of pyridine ester templates to direct selective steroid chlorination has also been investigated; the results indicate that the Cl atom coordinates to the N atom in pyridine before being relayed to a geometrically accessible substrate hydrogen.⁶ From a fundamental point of view, the sites of pyridine selectively attacked by Cl and the nature of the bonding, whether σ- or π-bonding, between Cl atom and pyridine have important implications.¹¹⁻¹³

Breslow et al. irradiated a solution of Cl₂ and C₅H₅N in CCl₄ with light at 355 nm and observed an absorption feature with λ_max = 334 nm;¹¹ they assigned this feature to charge-transfer band of 1-chloropyridinyl radical (C₅H₅N–Cl). They also performed calculations with the INDO/S (intermediate neglect of differential overlap) ROHF-CI (configuration interaction with restricted open-shell Hartree-Fock) method to predict an intense band near 318 nm correspond-

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constants for adduct formation and dissociation, determined from the forward and reverse rate coefficients, yield $\Delta H^\ddagger = 47.2 \pm 2.8$ kJ mol$^{-1}$. This experimental value of $\Delta H^\ddagger$ is consistent with that predicted quantum-chemically for the formation of a planar adduct with a $\sigma$-bond.$^{13,15}$

The matrix isolation technique is an excellent method to investigate IR spectra of reactive intermediates.$^{17,18}$ Because of the cage effect that inhibits the Cl from escaping from the original cage upon photolysis of its precursor such as Cl$_2$, photolytic reactions of Cl atom in noble-gas matrices are ineffective. Taking advantage of the diminished matrix cage effect of $p$-H$_2$, Raston and Anderson produced isolated CI atoms by photodissociation at 355 nm of Cl$_2$ trapped in solid $p$-H$_2$. We have employed this method to investigate reactions of Cl with molecules including CS$_2$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, trans-1,3-butadiene, and C$_2$H$_6$ in $p$-H$_2$ to identify radicals CISC$_2$, $^{20}$ 1-chloroethyl (CHCICH$_2$), $^{21}$ 2-chloropropyl (CH$_2$CHCICH$_3$), $^{22}$ 2-chloroethyl (CH$_2$CH$_2$Cl), $^{23}$ and trans-1-chloromethylyllyl (CH$_2$CHCHCH$_2$Cl)$_2$ $^{24}$ that were difficult to produce in typical experiments either in the gaseous phase or in noble-gas matrices.

In this work, we extended the investigations to the reaction of CI with pyridine and report IR absorption spectra of the 1-chloropyridinyl (C$_5$H$_5$N–CI) radical produced from addition of CI to pyridine selectively onto the N-site.

II. EXPERIMENTS

The details of the $p$-H$_2$ matrix isolation apparatus have been described in Refs. 21 and 22. In brief, a gold-plated copper block, maintained at 3.2 K with a closed-cycle refrigerator system (Janis RKD-415), served as both a cold substrate for the matrix and a mirror to reflect the incident IR beam to the detector. The C$_5$H$_5$N/$p$-H$_2$ (1/3000–1/3200) mixture and Cl$_2$ were co-deposited over a period of 8–11 h. The flow rate of the C$_5$H$_5$N/$p$-H$_2$ mixture was maintained at 10–12 nmol h$^{-1}$ and the flow rate of Cl$_2$ was maintained at 3–4 μmol h$^{-1}$ to achieve a molar ratio of Cl$_2$:C$_5$H$_5$N:$p$-H$_2$ $\equiv$ 3:1:3200.

After deposition the matrix was typically annealed at 4.5 K for 5 min to enhance the production of a complex between Cl$_2$ and C$_5$H$_5$N. To produce Cl atoms for reaction with C$_5$H$_5$N, we irradiated the matrix with ultraviolet light at 365 ± 10 nm from a light-emitting diode (Honey UV Technology, 375 mW) for 3 h. Following the photolysis at 365 nm, the matrix was annealed to 5.1 K for 3 min to induce further reaction.

Infrared absorption spectra were recorded with a Fourier-transform infrared FTIR spectrometer (BOMEM, D8) equipped with a KBr beam splitter and a HgCdTe detector cooled to 77 K. Interferograms were averaged over 600 scans to yield spectra in the range 400–4000 cm$^{-1}$ at spectral resolution 0.25 cm$^{-1}$. Because excitation of the solid $p$-H$_2$ with IR light in the range 4000–5000 cm$^{-1}$ induces reactions of Cl atoms with $p$-H$_2$ to form HCl $^{25,26}$ we placed an IR filter with truncation wavelength at 2.4 μm (Andover Co.) before the entrance window of the matrix system for IR beam during acquisition of spectral data so as to avoid the reaction of Cl with H$_2$.

To confirm the observation of the C$_5$H$_5$N--HCl complex as a product, in a separate experiment, we co-deposited C$_5$H$_5$N/$p$-H$_2$ and HCl/$p$-H$_2$ mixtures at 3.2 K and record the IR spectra. Before deposition, gaseous HCl was prepared in a separate flask containing a mixture of Cl$_2$/H$_2$ (1/2400) by irradiation with light at 365 nm to initiate the reaction Cl$_2$ + H$_2$ $\rightarrow$ 2 HCl.

Para-H$_2$ was synthesized by catalytic conversion of normal H$_2$ at low temperature. In this method, $n$-H$_2$ (99.999%, Scott Specialty Gases) was passed through a trap at 77 K and a copper coil filled with Fe(OH)$_3$ catalyst (catalyst grade, 30-50 mesh, Sigma-Aldrich) that was cooled with a closed-cycle refrigerator (Advanced Research System, DE204AF). The efficiency of conversion was controlled by the temperature of the catalyst. At conversion temperature 12–13 K, the concentration of $o$-H$_2$ is less than 100 ppm according to the Boltzmann distribution. Cl$_2$ (99.9%, Air Products and Chemicals) was used without further purification. Pyridine (Sigma-Aldrich, 99.8%) was distilled over KOH and degassed for several minutes to remove possible impurities.

III. COMPUTATIONAL METHOD

To characterize the complexes between C$_5$H$_5$N and Cl$_2$ molecules and to identify possible reaction products between CI atom and C$_5$H$_5$N, the equilibrium structures, vibrational wavenumbers, IR intensities, and energies of possible products were calculated with the GAUSSIAN 09 program. We employed the B3PW91 density-functional theory, which includes the three-parameter hybrid exchange functional of Becke $^{28}$ and gradient-corrected correlation functional of Perdew and Wang. The McLean-Chandler basis sets for second-row atoms including $p$, $d$, and diffuse functions, designated 6-311++G(2d, 2p), were used. Analytic first and second derivatives were applied for geometry optimization and vibrational wavenumbers at each stationary point. The anharmonic effects were calculated with a second-order perturbation approach using an effective finite-difference evaluation of the third and semidiagonal fourth derivatives.

A. $\sigma$- and $\pi$-bonded complexes of C$_5$H$_5$N–Cl$_2$

The structural parameters of $\sigma$- and $\pi$-bonded C$_5$H$_5$N–Cl$_2$ complexes, C$_5$H$_5$N, and Cl$_2$, optimized with the B3PW91/6-311++G(2d, 2p) method are shown in Fig. 1; those predicted previously with the MP2/aug-cc-pVZD method $^{31}$ are listed parenthetically. These structures are consistent with reported structures except the position of the Cl$_2$ molecule in the $\pi$-bonded C$_5$H$_5$N–Cl$_2$ complex. Wang et al. $^{31}$ found that Cl$_2$ points towards the center of the C=C double bond in the $\pi$-bonded C$_5$H$_5$N–Cl$_2$ complex, whereas our results indicate that it points towards the meta-carbon atom of C$_5$H$_5$N at 99.6° with respect to the molecular plane of pyridine. According to their calculations of CCSD(T)/aug-cc-pVZD using the full counterpoise method to correct for the effect of basis-set superposition error, the most stable structure of the C$_5$H$_5$N–Cl$_2$ complex is a $\sigma$-bonded planar structure with energy $-16.8$ ($-32.5$ before correction) kJ mol$^{-1}$ relative to Cl$_2$ + C$_5$H$_5$N. The $\pi$-complex is predicted to be $-5.6$ ($-15.4$ before correction) kJ mol$^{-1}$ relative to Cl$_2$ + C$_5$H$_5$N. Our values of $-27.9$ and
FIG. 1. Geometries and relative energies (in kJ mol$^{-1}$, zero-point energy corrected) of (a) C$_5$H$_5$N + Cl$_2$, (b) $\sigma$-C$_5$H$_5$N–Cl$_2$, and (c) $\pi$-C$_5$H$_5$N–Cl$_2$ optimized with the B3PW91/6-311$^{++}$G(2d, 2p) method. Bond distances are in Å and bond angles in degrees. Reported parameters predicted with the MP2/aug-cc-pVQZ method (Ref. 31) are listed in parentheses.

$-1.6$ kJ mol$^{-1}$ for the $\sigma$- and $\pi$-complex of C$_5$H$_5$N–Cl$_2$, respectively, show a similar trend.

The N–Cl distance in the $\sigma$-complex of C$_5$H$_5$N–Cl$_2$ is $2.349$ Å, consistent with the literature value of $2.261$ Å; the distance between Cl and the pyridine plane in the $\pi$-complex was reported to be $2.261$ Å. At the B3PW91/6-311$^{++}$G(2d, 2p) level of theory, the anharmonic vibrational wavenumbers for $\sigma$-bonded C$_5$H$_5$N–Cl$_2$ with IR intensities greater than $30$ km mol$^{-1}$ are predicted to be near $1593, 1455, 1217, 1075, 1014, 752, 625$, and $425$ cm$^{-1}$, whereas those of $\pi$-bonded C$_5$H$_5$N–Cl$_2$ are near $1589, 1446, 704$, and $525$ cm$^{-1}$. A complete list of harmonic and anharmonic vibrational wavenumbers of both complexes appears in Table I.

The spectral pattern of the predicted IR spectrum of $\pi$-bonded C$_5$H$_5$N–Cl$_2$ is similar to that of C$_5$H$_5$N in terms of line positions and relative IR intensities except a new line near $425$ cm$^{-1}$, with an intensity pattern distinct from that of C$_5$H$_5$N.

B. 1-chloropyridinyl (C$_5$H$_5$N–Cl) radical

The 1-chloropyridinyl (C$_5$H$_5$N–Cl) radical was calculated to be the most stable isomer from Cl + C$_5$H$_5$N, with a stabilization energy of $\sim 52$ kJ mol$^{-1}$ (Ref. 15) that is consistent with the experimental result of $\Delta H^\circ_{298} = 47.2 \pm 2.8$ kJ mol$^{-1}$. The geometry of the C$_5$H$_5$N–Cl radical computed with the B3PW91/6-311++G(2d, 2p) method is shown in Fig. 2(a). This geometry is similar to that predicted using the MP2(full)/6-311G(d)13 and the BB1K/6-31+G(d, p) methods; parameters of the latter are shown in parentheses for comparison. The N–Cl bond distance, $2.366$ Å, is

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similar to the corresponding value in the \( \sigma \)-bonded C5H5N–Cl2 complex. The anharmonic vibrational wavenumbers for modes of C5H5N–Cl2 with IR intensities greater than 15 km mol\(^{-1}\) are predicted to be near 3067, 1455, 1206, 1001, 748, and 692 cm\(^{-1}\). Harmonic and anharmonic vibrational wavenumbers of C5H5N–Cl2 are listed in Table II.

### C. 2-, 3-, and 4-chloropyridinyl (ClC5H5N) radicals

The geometries of 2-, 3-, and 4-chloropyridinyl (ClC5H5N) radicals computed with the B3PW91/6-311++G(2d, 2p) method are shown in Figs. 2(b)–2(d). Although the C–Cl bond distances, 1.902–1.948 Å, of these radicals are smaller than the N–Cl bond length of 2.366 Å in C5H5N–Cl, the energies of 2-, 3-, and 4-ClC5H5N are 31, 25, and 36 kJ mol\(^{-1}\) greater than that of C5H5N–Cl, presumably because the \( \sigma \)-bond between the Cl and the C atoms suppresses the aromaticity. Parveen and Chandra reported that \( \Delta H \) for formation of 2-, 3-, and 4-ClC5H5N are 32, 27, and 37 kJ mol\(^{-1}\) larger than that of C5H5N–Cl,\(^{15}\) in agreement with our results. The harmonic and anharmonic vibrational wavenumbers of 2-, 3-, and 4-ClC5H5N radicals are listed in Table II. According to calculations, the C–Cl stretching modes are predicted to be near 282, 210, and 270 cm\(^{-1}\) for 2-, 3-, and 4-ClC5H5N, respectively, beyond our detection range. The most intense lines are predicted near 743, 752, and 756 cm\(^{-1}\) for 2-, 3-, and 4-ClC5H5N, respectively; they are about 50 cm\(^{-1}\) greater than the wavenumber of the corresponding line of C5H5N–Cl near 692 cm\(^{-1}\).
D. 2-, 3-, and 4-pyridyl radicals (C₅H₄N)

Pyridyl (C₅H₄N) radicals might be produced via H-abstraction reaction of C₅H₅N by the Cl atom. The geometries of 2-, 3-, and 4-pyridyl radicals, predicted with the B3PW91/6-311+G(2d, 2p) method, are presented in Fig. S1 (supplementary material). The 2-pyridyl radical is found to be the most stable of the three pyridyl radicals, consistent with reported findings. The barrier for the Cl + C₅H₅N abstraction to produce 2-, 3-, and 4-C₅H₄N was predicted to be 13, 44, and 37 kJ mol⁻¹, respectively, with the B1K/6-31+G(d,p) method. The anharmonic vibrational wavenumbers for modes of 2-C₅H₄N with IR intensities greater than 20 km mol⁻¹ are predicted to be near 3044, 1619, 1556, 1397, 1054, 942, 739, and 570 cm⁻¹ with the B3PW91/6-311++G(2d, 2p) method. A complete list of the harmonic and anharmonic vibrational wavenumbers and relative IR intensities predicted for 2-, 3-, and 4-pyridyl radicals is available in supplementary material (Table S1).

IV. EXPERIMENTAL RESULTS

A. Formation of the C₅H₅N–Cl₂ complex in p-H₂

The IR spectrum of C₅H₅N in p-H₂ (1/3200) at 3.2 K in the spectral regions 420–780, 980–1280, 1400–1620, and 2980–3140 cm⁻¹ is presented in Fig. 3(a). It contains intense lines at 3084.6, 3039.0, 3007.0, 1598.5, 1582.9, 1579.5, 1483.2, 1440.8, 1217.7, 1031.9, 991.3, 744.2, 701.6, and 601.8 cm⁻¹; a complete list is included in Table I. These line positions are in agreement with those of gaseous C₅H₅N (Ref. 36) and C₅H₅N isolated in N₂ (Ref. 37) and Ar matrices reported previously.

### Table II. Comparison of observed vibrational wavenumbers (in cm⁻¹) and relative IR intensities of C₅H₅N–Cl with harmonic and anharmonic vibrational wavenumbers and relative IR intensities of C₅H₅N for modes of 2-C₅H₅N with IR intensities greater than 20 km mol⁻¹.

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<th>Mode</th>
<th>p-H₂</th>
<th>C₅H₅N–Cl²</th>
<th>2-C₅H₅N–Cl²</th>
<th>3-C₅H₅N–Cl²</th>
<th>4-C₅H₅N–Cl²</th>
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<td>v₁</td>
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*The order of modes follows the predicted anharmonic vibrational wavenumbers.

absorption to produce 2-, 3-, and 4-ClC₅H₅N, respectively.
When a mixture of Cl2/C5H5N/p-H2 (3/1/3200) was deposited at 3.2 K, new lines appear; their intensities increase upon annealing to 4.5 K for 5 min, as shown in Fig. 3(b). For clarity in showing the new lines induced by the presence of Cl2, we stripped lines due to isolated C5H5N (Fig. 3(a)) from the spectrum in Fig. 3(b) to yield the difference spectrum in Fig. 3(c). These new features with intense ones at 3091.4, 3047.2, 1591.8, 1446.7, 1212.7, 1070.3, 1003.7, 746.2, 699.0, 616.2, and 458.4 cm$^{-1}$ are assigned to the $\sigma$-bonded C5H5N–Cl2 complex, to be discussed in Sec. VA. A complete list of vibrational wavenumbers and relative IR intensities of these new features is presented in Table I. If we assume that the predicted IR intensities of C5H5N and C5H5N–Cl2 are reliable, we estimate that, according to Fig. 3(b), the mixing ratio of [C5H5N]:[C5H5N–Cl2] is approximately 1.0:0.6.

B. Photolysis of Cl2/C5H5N/p-H2 matrices

Upon irradiation of a Cl2/C5H5N/p-H2 matrix with light at 365 nm, the intensities of IR lines due to C5H5N and C5H5N–Cl2 complexes decreased, and new features in several groups appeared. These features are expected to result from reactions between Cl atom and C5H5N. A difference spectrum obtained on subtracting the spectrum of a Cl2/C5H5N/p-H2 (3/1/3200) matrix recorded upon deposition, followed by annealing at 4.5 K for 5 min and irradiation with 365 nm light for 3 h, from that recorded after subsequent annealing at 5.1 K for 3 min is presented in Fig. 4(b); lines pointing upwards indicate production; downward lines due to destruction of the precursors are suppressed. For comparison, the spectrum of a Cl2/C5H5N/p-H2 (3/1/3200) matrix recorded upon deposition at 3.2 K for 11 h followed by annealing at 4.5 K for 5 min is shown in Fig. 4(a). In the difference spectrum shown in Fig. 4(b), several lines of C5H5N and C5H5N–Cl2 show first-derivative shapes because of small shifts in line positions and changes in line shape upon photolysis and annealing.

As the IR intensities of new features remained small even after prolonged irradiation we deduced that the photoproducts underwent further photodecomposition. The greatest intensity of new features was attained upon annealing. To illustrate this condition, we show a difference spectrum obtained on subtracting the spectrum in Fig. 4(b) from that recorded upon further irradiation of the matrix at 365 nm for 12 min. Lines at 3075.9, 1449.7, 1200.6, 1148.8, 1069.3, 1017.4, 742.9, and 688.7 cm$^{-1}$ were produced upon annealing following 365-nm irradiation (upward pointing in Fig. 4(b)), but decreased in intensity upon further irradiation at 365 nm (downward pointing in Fig. 4(c)). These lines are denoted group A and indicated with “A” in Fig. 4. In the CH-stretching region, because of the severe overlap with absorption lines of the precursors, only one intense line is clearly identified at 3075.9 cm$^{-1}$. Two additional lines at 3058.3 and 3064.1 cm$^{-1}$ might also belong to the same group, because they show a similar trend (upward in Fig. 4(b) and downward in Fig. 4(c)), but parent absorption might interfere with the intensity ratios in these traces. These lines in group A are assigned to the 1-chloropyridinyl (C5H5N–Cl) radical, to be discussed in Sec. VB. The vibrational wavenumbers and relative IR intensities of these new features are listed in Table II.
FIG. 4. (a) Absorption spectrum of a Cl$_2$/C$_5$H$_5$N/p-H$_2$ (3/1/3200) matrix deposited at 3.2 K for 11 h and annealed at 4.5 K for 5 min. (b) Difference spectrum of the matrix after irradiation at 365 nm for 3 h, followed by annealing at 5.1 K for 3 min. (c) Difference spectrum of the matrix after further photolysis at 365 nm for 12 min. All experimental spectra were recorded at resolution 0.25 cm$^{-1}$. Lines marked with “*” are assigned to the σ-C$_5$H$_5$N–Cl$_2$ complex. Lines marked with “A” and “B” are assigned to C$_5$H$_5$N–Cl and C$_5$H$_5$N–HCl complex, respectively.

When we assume that the predicted IR intensities of C$_5$H$_5$N, C$_5$H$_5$N–Cl$_2$, and C$_5$H$_5$N–Cl are correct, we estimate the variation in mixing ratios $\Delta_1$[C$_5$H$_5$N]:$\Delta_1$[C$_5$H$_5$N–Cl$_2$]:$\Delta_1$[C$_5$H$_5$N–Cl] to be approximately $-(1.0 \pm 0.4)$:$-(0.05 \pm 0.01)$:$-(0.07 \pm 0.01)$ after annealing (Fig. 4(b)) and $\Delta_2$[C$_5$H$_5$N]:$\Delta_2$[C$_5$H$_5$N–Cl$_2$]:$\Delta_2$[C$_5$H$_5$N–Cl] to be approximately $-(1.0 \pm 0.4)$:$-(0.27 \pm 0.05)$:$-(0.43 \pm 0.02)$ after secondary photolysis (Fig. 4(c)). Some C$_5$H$_5$N might have evaporated upon annealing.

Lines in a second group, produced after photolysis and further increased in intensity upon annealing at 5.1 K, showed little change in intensity upon further irradiation at 365 nm, and are indicated with “B” in Fig. 4(b) and termed group B. Lines in group B include a broad feature near 904.5 cm$^{-1}$ and a line near 1052.1 cm$^{-1}$. Barnes et al. reported intense lines at 840 and 1050 cm$^{-1}$ and assigned them to the antisymmetric stretching and bending modes of the N–H–Cl moiety of C$_5$H$_5$N–HCl in solid Ar, respectively. Subsequent experiments confirmed this experimental result and reported lines at 1491.0, 1072.0, 1051.0, and 838.0 cm$^{-1}$ for C$_5$H$_5$N–HCl in solid Ar. To confirm the assignment, a separate experiment in which C$_5$H$_5$N and HCl were co-deposited with p-H$_2$ (C$_5$H$_5$N/HCl/p-H$_2$ = 1/1/2400) at 3.2 K, as shown in Fig. S2 (supplementary material), lines at 1491.8, 1455.4, 1066.4, 1052.3, and 904.5 cm$^{-1}$ are assigned to C$_5$H$_5$N–HCl in solid p-H$_2$. The two intense lines in group B are nearly identical to those observed for C$_5$H$_5$N–HCl in a p-H$_2$ matrix, we assigned these features to the C$_5$H$_5$N–HCl complex.

V. DISCUSSION

A. Assignment of lines of the σ-bonded C$_5$H$_5$N–Cl$_2$ complex

There is no report of identification of C$_5$H$_5$N–Cl$_2$ complexes with IR spectra, but Kimel’fel’d et al. reported Raman spectra of Cl$_2$ and Br$_2$ complexes with several amines including C$_5$H$_5$N at 77 K; a broad line at 440 cm$^{-1}$ was reported for C$_5$H$_5$N–Cl$_2$. Rubenacker et al. measured nuclear-quadrupole-resonance spectra of pyridine-halogen complexes including C$_5$H$_5$N–Cl$_2$ at 77 K and proposed that this complex is ionic. As described in Sec. III A, the σ-bonded C$_5$H$_5$N–Cl$_2$ complex is more stable than the π-bonded complex. Wang et al. reported that, according to their calculations of $\Delta G$, the formation of the σ-bonded C$_5$H$_5$N–Cl$_2$ complex but not the π-bonded complex is spontaneous at 200 K.

Upon co-deposition of Cl$_2$ with pyridine in p-H$_2$, we observed many new features (Fig. 3(c)) as compared with the spectrum of C$_5$H$_5$N/p-H$_2$ at 3.2 K (Fig. 3(a)). The intensity of these lines increases significantly upon annealing, consistent with the expectation that these lines are due to the formation of a complex between C$_5$H$_5$N and Cl$_2$. The positions of most newly observed lines are similar to those of pyridine, but lines at 458.4, 616.2, and 1003.7 cm$^{-1}$ are distinct from those of C$_5$H$_5$N.

For comparison, we plot the simulated IR spectra of σ-bonded C$_5$H$_5$N–Cl$_2$ complex, π-bonded C$_5$H$_5$N–Cl$_2$ complex, and C$_5$H$_5$N in Figs. 3(d) and 3(e); the
spectra were simulated according to the anharmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d, 2p) method and a spectral width of 0.25 cm$^{-1}$. The wavenumbers of $\pi$-bonded C$_5$H$_5$N–Cl$_2$ are similar to those of C$_5$H$_5$N except an enhanced feature near 534 cm$^{-1}$ that is associated with the CI–Cl stretching vibrational mode. In contrast, the spectrum of $\sigma$-bonded C$_5$H$_5$N–Cl$_2$ shows more significant spectral shifts and two significantly enhanced features near 422 (Cl–Cl stretching mode) and 632 cm$^{-1}$ (in-plane ring deformation mode).

Observed new features with intense ones at 3091.4, 1591.8, 1446.7, 1212.7, 1070.3, 1003.7, 746.2, 699.0, 616.2, and 458.4 cm$^{-1}$ agree satisfactorily with lines predicted for the $\sigma$-bonded C$_5$H$_5$N–Cl$_2$ in both wavenumbers and relative intensities, as shown in Figs. 3(c) and 3(d). Relative to absorption lines of C$_5$H$_5$N, most lines are blueshifted, except lines at 1212.7, 1070.3, and 699.0 cm$^{-1}$ that are redshifted, consistent with theoretical predictions of the direction of shifts (Table I). In the region below 500 cm$^{-1}$ a unique broad feature at 458.4 cm$^{-1}$ with full-width at half maximum (FWHM) of $\sim$7.2 cm$^{-1}$ was observed and is assigned to the Cl–Cl stretching mode of C$_5$H$_5$N–Cl$_2$; this mode was predicted to have harmonic (anharmonic) vibrational wavenumbers near 422 (425) cm$^{-1}$. That the width of this spectral line is much larger than that of other lines might indicate that a distribution of N–Cl–Cl angles is present in the complex. The assignments of some lines in the 3000–3100 cm$^{-1}$ region are tentative because of the similarity in vibrational wavenumbers and large anharmonicity associated with these modes and possible interference from the combination bands. Some lines are missing because of the severe overlap with absorption lines of C$_5$H$_5$N. For lines below 2000 cm$^{-1}$, the average deviation between observed and predicted anharmonic vibrational wavenumbers is 8.9 cm$^{-1}$, with a maximum deviation of 33 cm$^{-1}$ for the Cl–Cl stretching mode at 425 cm$^{-1}$.

Considering the agreement in positions and relative IR intensities between observed and predicted lines for the $\sigma$-bonded C$_5$H$_5$N–Cl$_2$ complex, the absence of a unique feature near 530 cm$^{-1}$ predicted for the $\pi$-bonded complex, and the calculated thermochemistry, we assigned these new features to the $\sigma$-bonded C$_5$H$_5$N–Cl$_2$ complex.

### B. Assignment of lines in group A to the 1-chloropyridinyl radical (C$_5$H$_5$N–Cl)

New lines in group A appeared upon annealing of a matrix of Cl$_2$/C$_5$H$_5$N/p-$\text{H}_2$ irradiated at 365 nm. Because photons at 365 nm dissociate only Cl$_2$ to produce Cl, not pyridine, we expect that the species produced upon annealing result from the reaction of Cl and pyridine via a barrierless path. During photolysis the intensities of lines in group A remain small, attributed to secondary photolysis of C$_5$H$_5$N–Cl. This reaction is supported by the observation of diminished intensity after further irradiation of the annealed matrix for 12 min, as shown in Fig. 4(c).

Although the addition of Cl to the N-atom site of pyridine is predicted to be the only spontaneous process near 300 K, we cannot exclude the possibility that addition of Cl to the ring carbon atoms at 2-, 3-, and 4-positions occurs at 5 K. The products of H-abstraction to form HCl + C$_5$H$_5$N, although unlikely to have a major contribution in the matrix near 3 K, should also be considered.

In Fig. 5(a) we reproduce the difference spectrum upon annealing at 5.1 K for 3 min of the Cl$_2$/C$_5$H$_5$N/p-$\text{H}_2$ (3.0/1.0/3200) matrix previously irradiated at 365 nm. Lines of group A are marked as “A” and the regions interfered by intense absorption of C$_5$H$_5$N and C$_5$H$_5$N–Cl$_2$ are marked with grey. In Figs. 5(b)–5(e) we plot the simulated IR spectra of radicals 1-chloropyridinyl (C$_5$H$_5$N–Cl), 2-, 3-, and 4-chloropyridinyl (ClC$_5$H$_5$N), respectively; the spectra were simulated according to the anharmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d, 2p) method and a spectral width of 0.25 cm$^{-1}$. The spectra of all three isomers of ClC$_5$H$_5$N are distinct because the C–Cl bonding at various sites of carbon has distinct effects on the bonding of the carbon ring. The simulated spectrum of C$_5$H$_5$N–Cl most resembles the spectrum of C$_5$H$_5$N, presumably because the weak interaction of Cl with the lone pair of the N atom least perturbs the structure of pyridine.

The observed wavenumbers and relative intensities of lines are in satisfactory agreement with those calculated for the C$_5$H$_5$N–Cl radical, but not with any of the 2-, 3-, and 4-chloropyridinyl (ClC$_5$H$_5$N) radicals, as illustrated in Fig. 5 and listed in Table II. The three most intense lines were observed at 1449.7, 742.9, and 688.7 cm$^{-1}$, near those predicted at 1455 (coupled C–C stretching and C–H in-plane bending mode), 748 (C–H out-of-plane bending mode), and 692 cm$^{-1}$ (C–H out-of-plane mode). The N–Cl stretching mode was predicted to be near 194 cm$^{-1}$, beyond our detection range. Assignments in the CH-stretching region are tentative because several modes were predicted to have similar vibrational wavenumbers and the anharmonicity correction altered the order of these modes. For lines below 2000 cm$^{-1}$, the average deviation between observed and predicted anharmonic vibrational wavenumbers is 7.2 cm$^{-1}$, with a maximum of 16.4 cm$^{-1}$ for the in-plane ring deformation mode ($v_{18}$) at 1017.4 cm$^{-1}$. The most intense line at 688.7 cm$^{-1}$ has a width (FWHM) of 1.7 cm$^{-1}$, larger than for other lines of this species. One possible reason is that, according to the quantum-chemical calculations, this mode involves motion that changes the distance between N and Cl and perhaps the potential energy surface with respect to the N–Cl distance is relatively flat. These observed lines in group A do not match those predicted for any H-abstraction product 2- or 3- or 4-C$_5$H$_5$N either, as shown in Table SI (supplementary material).

Considering the observed photolytic and annealing behavior, the agreement in wavenumber and relative IR intensity between lines observed and predicted for the C$_5$H$_5$N–Cl radical, the absence of some unique features of 2-, 3-, and 4-chloropyridinyl (ClC$_5$H$_5$N), and the calculated thermochemistry, we assign these new features in group A to the N-pyridinyl radical (C$_5$H$_5$N–Cl).
C. Reaction mechanisms in solid \( p\)-H\(_2\)

Upon irradiation of a Cl\(_2\)/C\(_5\)H\(_5\)N/\( p\)-H\(_2\) matrix at 365 nm, the initial process is the dissociation of Cl\(_2\) molecules to form Cl atoms. The production of isolated Cl atoms was confirmed with the observation of a line at 943.7 cm\(^{-1}\) associated with its spin-orbit transition \( ^2P_{1/2} \leftarrow ^2P_{3/2} \), consistent with the report by Raston and Anderson.\(^{19}\)

The Cl atoms might react with nearby C\(_5\)H\(_5\)N to form C\(_5\)H\(_5\)N–Cl or 2-, 3-, 4-ClC\(_5\)H\(_5\)N radicals; annealing of the matrix containing Cl and C\(_5\)H\(_5\)N enhances this reaction and avoids secondary photolysis. We observed C\(_5\)H\(_5\)N–Cl as the dominant product upon annealing, which is consistent with calculations that predict no barrier and greater exothermicity for formation of C\(_5\)H\(_5\)N–Cl adduct. In contrast, the energies of 2-, 3-, 4-ClC\(_5\)H\(_5\)N are greater than C\(_5\)H\(_5\)N–Cl by more than 26 kJ mol\(^{-1}\).\(^{15}\)

We observed that the intensities of lines of C\(_5\)H\(_5\)N–Cl attained maxima after irradiation at 365 nm for 1 h and remained nearly constant upon further irradiation. This behavior clearly indicates that the C\(_5\)H\(_5\)N–Cl radicals either react immediately with \( p\)-H\(_2\) or Cl atoms or undergo secondary decomposition. This photolytic destruction of C\(_5\)H\(_5\)N–Cl at 365 nm was confirmed with the difference spectrum recorded after irradiation of an annealed matrix for 12 min, as shown in Fig. 4(c). As we observed production of only C\(_5\)H\(_5\)N in this experiment, we conclude that C\(_5\)H\(_5\)N–Cl undergoes secondary photolysis at 365 nm to produce Cl and C\(_5\)H\(_5\)N.

Breslow \textit{et al.} observed an absorption with \( \lambda_{\text{max}} = 334 \) nm that was assigned to C\(_5\)H\(_5\)N–Cl in solution,\(^{11}\) supporting that the light of wavelength 365 ± 10 nm employed in this experiment was likely absorbed by C\(_5\)H\(_5\)N–Cl to induce photolysis.

The photodissociation of gaseous Cl\(_2\) at 365 nm can result in Cl atoms with 38 kJ mol\(^{-1}\) of translational energy,\(^{25, 26}\) which is ∼26 kJ mol\(^{-1}\) in the center-of-mass coordinates of the Cl + C\(_5\)H\(_5\)N system. This kinetic energy is greater than the barrier 13 kJ mol\(^{-1}\) predicted for formation of 2-C\(_5\)H\(_4\)N + HCl, but smaller than those, 44 and 37 kJ mol\(^{-1}\), predicted for formation of 3- and 4-C\(_5\)H\(_4\)N, respectively, with the BB1K/6-31++G(d,p) method.\(^{15}\) The fact that we observed no major line ascribable to 2-C\(_5\)H\(_4\)N indicates that either the kinetic energy of Cl was readily quenched before it could find a suitable attacking site to effect H-abstraction or 2-C\(_5\)H\(_4\)N reacts readily with H\(_2\) to form C\(_5\)H\(_5\)N. Further isotopic experiments are needed to distinguish these two possible channels.

VI. CONCLUSION

The reaction of Cl atoms with pyridine in solid \( p\)-H\(_2\) at 3.2 K has been investigated using matrix isolation IR absorption spectroscopy. The most stable planar \( \sigma \)-bonded C\(_5\)H\(_5\)N–Cl\(_2\) complex was identified in a matrix of Cl\(_2\)/C\(_5\)H\(_5\)N/\( p\)-H\(_2\) at 3.2 K; observed shifts in wavenumbers and relative intensities of the IR absorption lines of \( \sigma \)-C\(_5\)H\(_5\)N–Cl\(_2\) with respect to C\(_5\)H\(_5\)N isolated in solid \( p\)-H\(_2\) agree satisfactorily with
the results of quantum-chemical calculations. Upon annealing of the matrix sample Cl/C₅H₅N/p-H₂ (3/1/3200) irradiated with UV light at 365 nm, we observed 1-chloropyridinyl (C₅H₅N−Cl) radical as a major product. The assignments were made according to the expected chemistry, the predicted energy barriers for various reactions, and the anharmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d, 2p) method. No other isomeric product such as 2-, 3-, 4-CIC₅H₅N was identified.

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32. See supplementary material at http://dx.doi.org/10.1063/1.4789407 for geometries, relative energies, vibrational wavenumbers, and IR intensities of 2-, 3-, 4-CIC₅H₅N radicals optimized with the B3PW91/6-311++G(2d, 2p) method and spectrum of the C₅H₅N-HCl complex.