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Reactions between chlorine atom and acetylene in solid *para*-hydrogen: Infrared spectrum of the 1-chloroethyl radical

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We applied infrared matrix isolation spectroscopy to investigate the reactions between Cl atom and acetylene (C_2H_2) in a *para*-hydrogen (p-H_2) matrix at 3.2 K; Cl was produced via photodissociation at 365 nm of matrix-isolated Cl_2 *in situ*. The 1-chloroethyl radical ($\cdot CHClCH_3$) and chloroethene (C_2H_3Cl) are identified as the main products of the reaction Cl + C_2H_2 in solid p-H_2. IR absorption lines at 738.2, 1027.6, 1283.4, 1377.1, 1426.6, 1442.6, and 2861.2 cm^{-1} are assigned to the 1-chloroethyl radical. For the reaction of Cl + C_2D_2, lines due to the $\cdot CDClCH_2D$ radical and *trans*-CHDCDCl are observed; the former likely has a *syn*-conformation. These assignments are based on comparison of observed vibrational wavenumbers and ^{13}C- and D-isotopic shifts with those predicted with the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ methods. Our observation indicates that the primary addition product of Cl + C_2H_2, 2-chlorovinyl ($\cdot CHCHCl$) reacts readily with a neighboring p-H_2 molecule to form $\cdot CHClCH_3$ and C_2H_3Cl. Observation of $\cdot CDClCH_2D$ and *trans*-CHDCDCl from Cl + C_2D_2 further supports this conclusion. Although the reactivity of p-H_2 appears to be a disadvantage for making highly reactive free radicals in solid p-H_2, the formation of 1-chloroethyl radical indicates that this secondary reaction might be advantageous in producing radicals that are difficult to prepare from simple photolysis or bimolecular reactions *in situ*. *© 2011 American Institute of Physics*. [doi:10.1063/1.3653988]

I. INTRODUCTION

The reaction between Cl_2 and acetylene (ethyne, C_2H_2) is a prototype for addition reactions of halogen to carbon–carbon triple bonds in organic chemistry. The reaction is believed to proceed via a radical mechanism in which addition of a Cl atom to the triple bond initiates the reaction.[1] The reaction of Cl atom with C_2H_2 is reported to play an important role in their removal from the marine atmosphere and the polar troposphere;[2–4] the reaction serves also as a sink of Cl atoms in the stratosphere.[5–7]

The Cl + C_2H_2 reaction has been the subject of numerous experimental[4,8–14] and theoretical investigations.[1,10,15] These studies indicate that two initial processes, the addition of the Cl atom to C_2H_2 to form the 2-chlorovinyl radical ($\cdot CHCHCl$) and the abstraction of an H atom of C_2H_2 to form the ethynyl radical ($\cdot CCH$) and HCl, are possible for this reaction. The branching ratio of these two channels depends on pressure and temperature. The radical products subsequently undergo further reactions to form stable molecular products such as dichloroethene and higher chlorohydrocarbons. The infrared (IR) absorption experiments reported by Zhu and Yarwood[9] indicate that the photochlorination of gaseous C_2H_2 in N_2 produces *cis*-CHClCHCl (16%) and *trans*-CHClCHCl (84%).

Quantum-chemical calculations indicate that the addition reaction of Cl + C_2H_2 proceeds via a Cl-C_2H_2 complex of C_{2v} symmetry to form the 2-chlorovinyl radical, $\cdot CHCHCl$, with an exothermicity of 57−73 kJ mol^{-1}. The 2-chlorovinyl radical is predicted to have two isomers: *trans*-CHCHCl is more stable than *cis*-CHCHCl by ∼5 kJ mol^{-1} and the barrier for converting *cis*-CHCHCl to *trans*-CHCHCl is ∼16 kJ mol^{-1}.[15] The spectral identification of the 2-chlorovinyl radical remains unreported.

For reactions of C_2H_2 with small atoms such as H or F, IR absorption of the radical products of the addition reactions, $\cdot CHCH_2$ (see Ref. 16) and $\cdot CHCHF$,[17,18] isolated in noble-gas matrices were identified. These species were generated in noble-gas matrices via annealing-induced reactions or via co-deposition of C_2H_2 and F atoms produced in a microwave discharge. Preceding work indicates that the cage effects associated with conventional Ar or Ne matrices pose some limitation to study the reactions of Cl or Br atoms produced from ultraviolet (UV) photolysis of Cl_2 or Br_2 *in situ*. The Cl or Br atoms produced in these matrices cannot escape the original matrix cage easily; consequently the observed products typically involve the reaction of both halogen atoms.[19,20]

The use of solid *para*-hydrogen (p-H_2) as a matrix host has generated considerable interest in recent years because of the unique properties associated with this quantum solid.[21–24] The diminished matrix cage effect makes feasible investigations of free radicals via direct photolysis of precursors[25–27] or bimolecular reactions induced from photolysis *in situ*.[28–31] Raston and Anderson[32] employed laser emission at 355 nm to photodissociate Cl_2 trapped in solid p-H_2 at 2 K and produced isolated Cl atoms. It is thus expected that

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reaction of Cl with other small molecules might produce free radicals that are difficult to produce in noble-gas matrices. Our research group has demonstrated that irradiation of a $Cl_2/CS_2/p\text{-}H_2$ matrix with UV light at 340 nm results in reaction products containing only a single chlorine atom: ClSCS, ClCS, and ClSC.[28] Similarly, UV radiation of matrices $Cl_2/C_2H_4/p\text{-}H_2$ and Cl_2/propene/$p\text{-}H_2$ with light at 365 nm produces 2-chloroethyl ($\cdot CH_2CH_2Cl$)[29] and 2-chloropropyl ($\cdot CH_2CHClCH_3$) radicals,[30] respectively.

In this paper, we report IR absorption spectra of the reaction products resulting from UV irradiation of $p\text{-}H_2$ matrices containing Cl_2 and C_2H_2 (or $^{13}C_2H_2$, C_2D_2); the addition product $\cdot CHCHCl$ reacts readily with neighboring $p\text{-}H_2$ to form 1-chloroethyl radicals ($\cdot CHClCH_3$) and chloroethene (C_2H_3Cl) as major products.

II. EXPERIMENTS

A gold-plated copper block, maintained at 3.2 K, served as both a cold substrate for the matrix sample and a mirror to reflect the incident IR beam to the detector.[28,33] The low temperature was achieved with a closed-cycle refrigerator system (Janis RKD-415). Typically, gaseous mixtures of $C_2H_2/p\text{-}H_2$ and $Cl_2/p\text{-}H_2$ were co-deposited over a period of 5−8 h at flow rates of 7−8 mmol h^{-1}. The mixing ratio of the $C_2H_2/p\text{-}H_2$ mixture was 1/1000−1/2000, and that of $Cl_2/p\text{-}H_2$ mixture was 1/600−1/4000.

IR absorption spectra were recorded with a Fourier-transform IR spectrometer (Bomem, DA8) equipped with a KBr beam splitter and a HgCdTe detector cooled to 77 K to cover the spectral range 500–5000 cm^{-1}. Typically, 500 scans at 0.25 cm^{-1} resolution were co-added at each stage of the experiment. All spectra were recorded at 3.2 K. Excitation of the solid $p\text{-}H_2$ with IR light in the range 4000–5000 cm^{-1} induces reactions of Cl atoms with $p\text{-}H_2$ to form HCl.[34,35] In our experiments when Cl atoms were present in the $p\text{-}H_2$ matrix, an IR filter with a cutoff wavelength at 2.4 μm (Andover Co.) was therefore used when recording the IR spectra to avoid the reaction of $Cl + H_2$.

In some experiments, after the initial co-deposition of the $Cl_2/p\text{-}H_2$ and $C_2H_2/p\text{-}H_2$ mixtures, the matrix was annealed at 4.3 K for up to 0.5 h to enhance production of the complex between Cl_2 and C_2H_2. To produce Cl atoms for reaction with C_2H_2, the $Cl_2/C_2H_2/p\text{-}H_2$ matrices were irradiated with light at 365 ± 10 nm from a light-emitting diode (Honle UV Technology, 375 mW) for 2–5 h. Following the photolysis at 365 nm, the matrix was sometimes annealed to 4.3 K to induce further reaction. Secondary photolysis was performed using one or more of the following light sources: a globar with a bandpass filter passing 3870–4980 cm^{-1} (W02296-7, OCLI Products), a low-pressure Hg lamp (Pen-Ray lamp, UVP) with or without a bandpass filter passing 254 ± 10 nm (ESCO Products), and a Zn lamp without a filter. The increase or decrease in line intensities in different extent observed after photolysis enables us to separate observed lines into various groups that are attributable to various products.

$p\text{-}H_2$ was produced by catalytic conversion at low temperature in which normal H_2 gas (99.9999%, Scott Specialty Gases) was passed through a copper coil filled with a hydrated iron (III) oxide catalyst (catalyst grade, 30−50 mesh, Sigma-Aldrich) that was cooled with a closed-cycle refrigerator (Advanced Research Systems, DE204AF). Before entering the coil containing the catalyst, the H_2 gas was passed through a trap cooled to 77 K. The efficiency of the conversion is controlled by the temperature of the catalyst, which was typically 13–14 K in these experiments. At this temperature, the mixing ratio of $o\text{-}H_2$ is less than 100 ppm according to the Boltzmann distribution.

III. RESULTS

A. Calculations on the C_2H_2-Cl_2 complex, 2-chlorovinyl ($\cdot$CHCHCl), and 1-chloroethyl ($\cdot CHClCH_3$) radicals

The equilibrium geometries, vibrational wavenumbers, IR intensities, and energies were calculated with the GAUSSIAN 09 program.[36] Our calculations are based on B3LYP density-functional theory[37,38] and the second-order Møller-Plesset perturbation theory (MP2).[39] Dunning's correlation-consistent polarized-valence double-zeta basis set augmented with *s*, *p*, *d*, and *f* functions (aug-cc-pVDZ) (Ref. 40) was used in both methods. Algebraic first derivatives were utilized in geometry optimization, and harmonic vibrational wavenumbers were calculated analytically at each stationary point. The anharmonic effects were calculated by second-order perturbation approach using effective finite difference evaluation of the third and semidiagonal fourth derivatives.

1. The C_2H_2-Cl_2 complex

The calculations predicted that the most stable structure of C_2H_2-Cl_2 is a T-shaped bπ-aσ complex.[41–44] The structural parameters predicted with the B3LYP/aug-cc-pVDZ method are shown in Fig. 1(a), and those predicted with the MP2/cc-pVDZ method are listed parenthetically. These structures are consistent with literature values. At the B3LYP/aug-cc-pVDZ level of theory, harmonic vibrational wavenumbers of C_2H_2-Cl_2 are predicted at 3518, 3414, 2052, 740, 727, 571, 556, and 480 cm^{-1}, whereas anharmonic vibrational wavenumbers are predicted at 3373, 3279, 2020, 763, 758, 767, 772, and 481 cm^{-1}. At the MP2/aug-cc-pVDZ level of theory, these values become 3512, 3424, 1938, 712, 701, 415, 394, and 512 cm^{-1}. Predicted harmonic and anharmonic vibrational wavenumbers and IR intensities of C_2H_2-Cl_2, $^{13}C_2H_2$-Cl_2, and C_2D_2-Cl_2 are compared with the experimental values in Table I.

2. 2-Chlorovinyl ($\cdot$CHCHCl) and 1-chlorovinyl ($\cdot CClCH_2$) radicals

The 1-chlorovinyl ($\cdot CClCH_2$) radical is predicted to be the most stable isomer of chlorovinyl radicals, with its energy smaller than that of *trans*-CHCHCl by 13.9, 12.7, and 12.4 kJ mol^{-1}, respectively, according to the B3LYP/aug-ccpVDZ, MP2/aug-ccpVDZ, and CCSD(T)/aug-ccpVDZ//CCSD/6-31G(d,p) methods.[15] However, 1-chlorovinyl cannot be produced directly from $Cl + C_2H_2$. Isomerization from

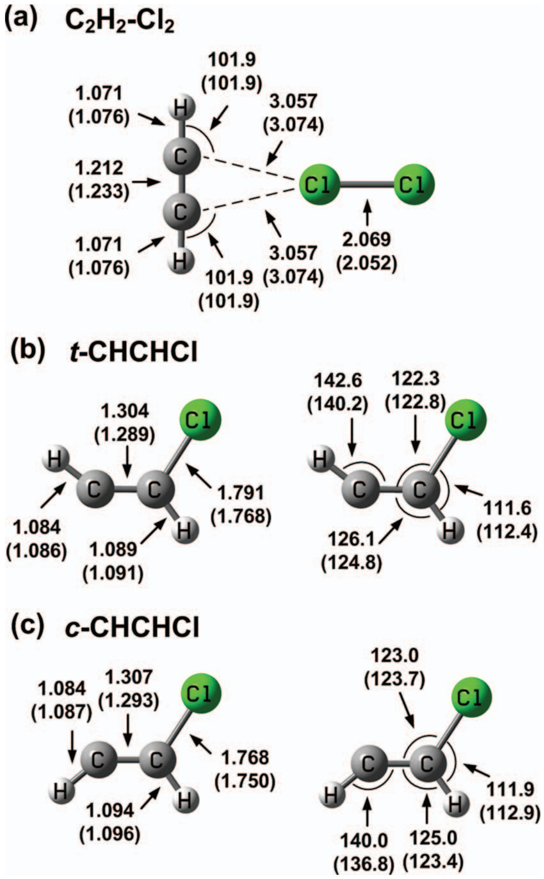

FIG. 1. Geometries of (a) the C_2H_2-Cl_2 complex, (b) *trans*-CHCHCl, and (c) *cis*-CHCHCl predicted with the B3LYP/aug-cc-pVDZ method. Corresponding values predicted with the MP2/aug-cc-pVDZ method are listed in parentheses. Bond distances are in Å and angles are in degrees.

trans-CHCHCl requires 186 kJ mol^{-1} as predicted with the CCSD(T)/aug-cc-pVDZ//CCSD/6-31G(d,p) method.[15]

The geometries of 2-chlorovinyl radicals, *trans*-CHCHCl and *cis*-CHCHCl, predicted with the B3LYP/aug-cc-pVDZ method are presented in Figs. 1(b) and 1(c), respectively. The structural parameters derived with the MP2 method are listed in parentheses for comparison. The energy differences after correction for zero-point energy (ZPE) of *trans*-CHCHCl and *cis*-CHCHCl, $E(cis) - E(trans)$, are 5.3, 4.1, 5.2, and 4.4 kJ mol^{-1}, respectively, according to the B3LYP/aug-ccpVDZ, MP2/aug-ccpVDZ, CCSD(T)/aug-ccpVDZ//CCSD/6-31G(d,p),[15] UCCSD(T)/6-311+G(2df,2p)//UMP2/6-31G(d,p)[1] methods.

Table II lists harmonic vibrational wavenumbers and IR intensities predicted for *trans*-CHCHCl and *cis*-CHCHCl with various levels of theory. The B3LYP/aug-cc-pVDZ method predicts that major IR lines of *trans*-CHCHCl are at 1637, 826, 783, and 639 cm^{-1} with intensities 45, 72, 93, and 39 km mol^{-1}, respectively. The major IR lines of *cis*-CHCHCl are predicted at 1635, 821, 618, and 578 cm^{-1} with intensities 46, 28, 64, and 60 km mol^{-1}, respectively.

3. The 1-chloroethyl ($\cdot$ $CHClCH_3$) radical

The geometries of the 1-chloroethyl radical computed in this work at the B3LYP/aug-cc-pVDZ levels are shown in Fig. 2(a); the structural parameters derived with the MP2/aug-cc-pVDZ method are listed in parentheses. They agree with the values reported by Brana *et al*.. using the QCISD/6-31G(d,p) method.[45] The harmonic vibrational wavenumbers and IR intensities predicted with the B3LYP and MP2/aug-cc-pVDZ methods for $\cdot CHClCH_3$ and $\cdot {}^{13}CHCl^{13}CH_3$ are listed in Table III.

Three stable conformers of $\cdot CDClCH_2D$ are shown in Fig. 2(b). We designate the conformation by the relative position of the two D atoms. The dihedral angles of the C*−C−D plane relative to the D−C*−C plane, in which C* indicates the carbon atom that bonds with the Cl atom and has an unpaired electron, are −25.8°, −146.0°, and 94.0° for *syn*-, *anticlinal*-, and *anti*-$CDClCH_2D$, respectively. These three conformers have similar energy, with the most stable conformation being *syn*, which is 0.09 and 0.28 kJ mol^{-1} more stable than *anticlinal* and *anti*, respectively, after taking into consideration the ZPE. Predicted vibrational wavenumbers and IR intensities of three conformers of $\cdot CDClCH_2D$ are listed in Table IV. Those of the three conformers of $\cdot CHClCHD_2$ and two of $\cdot CHDCHDCl$ are listed in Table S1, see supplementary material.[46]

B. Formation of the C_2H_2-Cl_2 complex in solid p-H_2

1. Experiments of Cl_2 + C_2H_2 in natural abundance

The infrared spectrum of C_2H_2 in p-H_2 at 3.2 K in the spectral region between 500 and 4000 cm^{-1} is characterized by a series of lines with the most intense feature (ν_5) at 733.8 cm^{-1} and weaker ones at 1331.6 ($\nu_4 + \nu_5$) cm^{-1}, 3279.4 (ν_3) cm^{-1}, and 3294.4 ($\nu_2 + \nu_4 + \nu_5$) cm^{-1}, in agreement with literature spectra of C_2H_2 in a supersonic jet[47] and isolated in Ar[48] and Kr.[49] In a more dilute C_2H_2 sample in solid p-H_2, the line at 733.8 cm^{-1} shifts to 738.5 cm^{-1}, as reported previously.[47]

When the p-H_2 matrix was doped with both C_2H_2 and Cl_2 a set of new lines unobserved in the C_2H_2/p-H_2 matrix appears; their intensity increases upon annealing to 4.3 K. These new features at 3276.0, 1968.8, 741.7, 732.2, 539.4, and 532.2 cm^{-1} are assigned to C_2H_2-Cl_2 complexes, consistent with lines at 3277, 1972, 776, and 527 cm^{-1} reported for C_2H_2-Cl_2 isolated in solid Ar.[41] Laursen and Pimentel[42] reported lines with similar wavenumbers for C_2H_2-Cl_2 upon irradiation at 237 nm of *cis*-1,2-$C_2H_2Cl_2$ and *trans*-1,2-$C_2H_2Cl_2$ in solid Xe, and at 239 nm of *cis*-1,1-$C_2H_2Cl_2$ isolated in solid Xe,[43] as listed in Table I.

These lines are consistent with theoretical predictions of vibrational wavenumbers of C_2H_2-Cl_2,[44] as listed in Table I; predicted anharmonic vibrational wavenumbers fit better. Activation of the originally forbidden C≡C stretching mode near 1968.8 cm^{-1} and the Cl−Cl stretching modes near 539.4 and 532.3 cm^{-1} is due to the interaction between Cl_2 and C_2H_2.

2. Experiments with the ^{13}C- and D-isotopic species

The vibrational wavenumbers of $^{13}C_2H_2$-Cl_2 and C_2D_2-Cl_2 observed experimentally and calculated with the B3LYP and MP2 methods are also summarized in Table I.

TABLE I. Comparison of experimentally observed wavenumbers (in cm^{-1}) with vibrational wavenumbers and IR intensities (in km mol^{-1}, listed parenthetically) predicted for C_2H_2-Cl_2, $^{13}C_2H_2$-Cl_2, and C_2D_2-Cl_2 with quantum-chemical calculations.

	Harmonic		Anharmonic	Experiments		
No.[a]	B3LYP/aug-cc-pVDZ	MP2/aug-cc-pVDZ	B3LYP/aug-cc-pVDZ	Ar matrix[b]	Xe matrix[c]	p-H_2 matrix
			C_2H_2-Cl_2			
ν_1	3517.8 (0.0)	3512.3 (0.5)	3373.2			
ν_2	3414.0 (110)	3424.5 (105)	3278.9	3277	3277.8[d] 3264.0	3276.0
ν_3	2051.7 (16.4)	1938.0 (3.8)	2020.1	1972		1968.8
ν_4	740.2 (134)	711.7 (123)	763.3[e]	776?	736.8	741.7
ν_5	727.1 (90.6)	701.2 (85.7)	757.6[e]		728.5	732.2
ν_6	570.5 (0.0)	414.8 (0.0)	766.9[e]			
ν_7	556.2 (0.0)	393.7 (0.0)	772.0[e]			
ν_8	479.6 (38.1)	512.2 (12.6)	480.6	527		539.4/532.2
			$^{13}C_2H_2$-Cl_2			
ν_1	3491.2 (0.0)	3488.8 (0.7)	3347.6			
ν_2	3403.6 (110)	3414.1 (105)	3268.1			3269.5
ν_3	1985.8 (15.8)	1873.5 (3.6)	1956.1			1905.2
ν_4	738.0 (132)	709.6 (121)	759.3[e]			739.7
ν_5	725.3 (89.4)	699.0 (85.3)	753.7[e]			729.4
ν_6	562.6 (0.0)	409.4 (0.0)	752.4[e]			
ν_7	547.9 (0.0)	387.6 (0.0)	757.6[e]			
ν_8	480.2 (40.4)	512.3 (12.7)	481.2			539.4/532.2
			C_2D_2-Cl_2			
ν_1	2816.0 (3.6)	2767.6 (0.0)	2730.8			
ν_2	2506.6 (58.0)	2514.3 (55.4)	2432.8		2424.4	2431.5
ν_3	1812.9 (11.7)	1739.1 (3.2)	1790.6			1759.4
ν_4	544.1 (70.1)	524.2 (47.2)	556.0[e]		543.3	547.8
ν_5	534.5 (47.2)	515.1 (45.4)	551.8[e]		537.4	542.8?
ν_6	471.0 (0.0)	339.2 (0.0)	607.4[e]			
ν_7	464.1 (0.0)	327.8 (0.0)	612.4[e]			
ν_8	479.7 (48.5)	510.9 (35.8)	480.3			538.7/531.5

[a] Low frequency modes $\nu_9-\nu_{12}$ are unlisted.

[b] From Ref. 41.

[c] From photolysis of CH_2CCl_2 (see Ref. 43). Also at 3277.1, 3264.4, 736.4, and 727.9 cm^{-1} (from photolysis of *cis*-CHClCHCl) and 3276.8. 3264.2, 736.4, 728.7, and 727.9 cm^{-1} (from photolysis of *trans*-CHClCHCl) (see Ref. 42).

[d] Split due to Fermi resonance with ($\nu_2+\nu_4+\nu_5$).

[e] Anharmonic vibrational wavenumbers of these modes are greater than harmonic wavenumbers; they might be unreliable and need further investigation.

Absorption lines of the $^{13}C_2H_2$-Cl_2 complex are similar to those of $^{12}C_2H_2$-Cl_2 except that some lines are slightly redshifted. The most intense line of C_2H_2-Cl_2 shifts from 741.7 to 739.7 cm^{-1} with a ^{13}C-isotopic ratio of 739.7/741.7 = 0.9973, defined as the ratio of the vibrational wavenumber of isotopic species to that of the natural species. This ratio is in agreement with the theoretical value of 759.3/763.3 = 0.9948 according to anharmonic vibrational wavenumbers predicted with the B3LYP/aug-cc-pVDZ method. The largest isotopic shift was observed for the C≡C stretching mode with the line of $^{12}C_2H_2$-Cl_2 at 1968.8 cm^{-1} shifts by 63.6 cm^{-1} to 1905.2 cm^{-1} for $^{13}C_2H_2$-Cl_2, in satisfactory agreement with the shift 64.0 cm^{-1} predicted with the B3LYP calculations. The experimental and calculated ^{13}C-isotopic ratios for this mode are 0.9677 and 0.9683, respectively.

The absorption spectrum of the C_2D_2-Cl_2 complex indicates that the line for the asymmetric C−H stretching mode of C_2H_2-Cl_2 shifts from 3276.0 to 2431.5 cm^{-1} with a D-isotopic shift of 844.5 cm^{-1}, in agreement with the theoretical value of 846.1 cm^{-1} according to anharmonic vibrational wavenumbers predicted with the B3LYP method. The line at 1968.8 cm^{-1} for the C≡C stretching mode of $^{12}C_2H_2$-Cl_2 shifts to 1759.4 cm^{-1} for C_2D_2-Cl_2. The D-isotopic shift of 209.4 cm^{-1} agrees satisfactorily with the predicted value of 229.5 cm^{-1}.

C. Photolysis of $Cl_2/C_2H_2/p$-H_2 matrices

1. *Experiments of Cl_2 + C_2H_2 in natural abundance*

Upon irradiation of a $Cl_2/C_2H_2/p$-H_2 matrix with light at 365 nm, the intensity of IR features due to C_2H_2 and C_2H_2-Cl_2 complexes decreased, and new features in several groups appeared. These new features are expected to belong to the reaction products between Cl atoms, produced via photolysis of Cl_2, and C_2H_2. A difference spectrum obtained on

TABLE II. Calculated harmonic vibrational wavenumbers (cm^{-1}) and IR intensities (km mol^{-1}, listed in parentheses) of *trans*-CHCHCl and *cis*-CHCHCl.

	trans-CHCHCl			*cis*-CHCHCl		
Mode	B3LYP[a]	MP2[a]	CCSD[b]	B3LYP[a]	MP2[a]	CCSD[b]
ν_1	3302 (11)	3348 (9)	3362	3294 (11)	3337 (10)	3357
ν_2	3212 (5)	3267 (9)	3295	3141 (6)	3210 (9)	3232
ν_3	1637 (45)	1861 (46)	1659	1635 (46)	1856 (48)	1667
ν_4	1203 (7)	1242 (9)	1290	1199 (6)	1237 (7)	1292
ν_5	826 (72)	984 (94)	893	618 (64)	747 (78)	684
ν_6	783 (93)	863 (95)	885	821 (28)	893 (20)	805
ν_7	643 (14)	815 (5)	723	764 (6)	939 (0)	920
ν_8[c]	639 (39)	721 (31)	667	578 (60)	665 (60)	659
ν_9	343 (12)	366 (7)	371	376 (5)	400 (5)	401
Ref.	This work	This work	15	This work	This work	15

[a] Calculated with the aug-cc-pVDZ basis set.

[b] Calculated with the 6-31G(d,p) basis set.

[c] For *cis*-CHCHCl this mode is coupled with the $H^{\alpha}CC$ bending mode.

subtracting the spectrum of a $Cl_2/C_2H_2/p$-H_2 (1/2/6000) matrix, deposited at 3.2 K for 7 h, from the spectrum recorded after irradiation at 365 nm for 5 h is presented in Fig. 3(a); lines pointing upwards indicate production. A difference spectrum obtained on subtracting the spectrum of a $Cl_2/C_2H_2/p$-H_2 (1/1/2000) matrix, deposited at 3.2 K for 5 h and annealed at 4.3 K for 0.5 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 3(b). The difference spectrum obtained after annealing of this irradiated matrix at 4.3 K for 0.5 h is shown in Fig. 3(c). The difference spectrum obtained after subsequent irradiation with light in spectral range 3870–4980 cm^{-1} is shown in Fig. 3(d). The IR irradiation of the matrix excites H_2 molecules and allows reaction of H_2 with Cl (Ref. 34) to produce HCl and H. The H atom thus produced and the vibrationally excited H_2 might react further with other radicals such as CHCHCl or molecules such as C_2H_2.

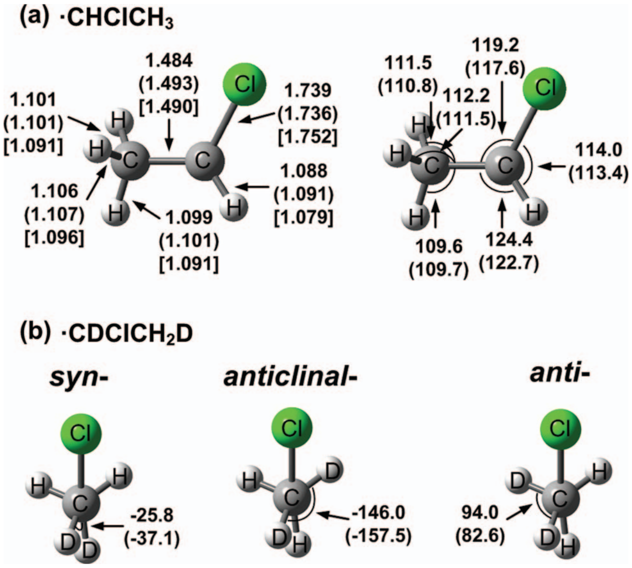

FIG. 2. (a) Geometries of $\cdot CHClCH_3$ predicted with the B3LYP/aug-cc-pVDZ method. Corresponding values predicted with the MP2/aug-cc-pVDZ method are listed in parentheses. Results predicted with the QCISD/6-31G(d,p) method (Ref. 45) are listed in brackets for comparison. Bond distances are in Å and angles are in degrees. (b) The dihedral angles of three conformers of $\cdot CDClCH_2D$.

These new features in Figs. 3(a) and 3(b) are separated into two major groups (A and X) and two minor ones (B and C) according to their behavior under secondary photolysis or annealing to 4.3 K, and also from the results of experiments in which larger concentrations of Cl_2 in the $Cl_2/C_2H_2/p$-H_2 mixture were used. The lines of group A, marked "A" in Fig. 3(a) and listed in Table V, are readily assigned to chloroethene, C_2H_3Cl, based on a comparison of the observed line positions with literature values[50] and a control experiment in which an authentic sample of C_2H_3Cl/p-H_2 was deposited at 3.2 K. The intensity of lines in this group increases when the matrix was irradiated with IR light, as indicated in Fig. 3(d).

The intense features marked as group X in Fig. 3(a) and listed in Table III appeared after irradiation of the matrix at 365 nm, but their intensities decreased slightly when the matrix was subsequently irradiated with IR light, as shown in Fig. 3(d). Weak lines at 3100.8, 2970.2, 2902.3 (all marked "X?"), and 1106.0 cm^{-1} (not shown) might be associated also with group X. This behavior indicates that these features are likely associated with an unstable species that reacts with vibrationally excited H_2 or H atoms. These lines of group X are assigned to the 1-chloroethyl ($\cdot CHClCH_3$) radical, to be discussed in Sec. IV A.

The lines of group B, as shown in Fig. 3(b) and listed in Table V, appeared after irradiation of the $Cl_2/C_2H_2/p$-H_2 (1/1/2000) matrix at 365 nm but their intensities are much smaller in a matrix with more diluted Cl_2, for which only lines at 1058.7 and 702.8 cm^{-1} are clearly visible in Fig. 3(a); their intensities remained nearly unchanged upon further IR irradiation. These features are readily assigned to 1,1-dichloroethane, $CHCl_2CH_3$, based on the literature spectra of this compound and the observation of enhanced intensity of lines in this group when an increased mixing ratio of Cl_2 in the $Cl_2/C_2H_2/p$-H_2 matrix was used.

Weak lines of group C at 1440.0 and 948.4 cm^{-1} are assigned to ν_7 and ν_{12} modes of C_2H_4, respectively, according to literature values[29,51] and our experiments with C_2H_4/p-H_2. As shown in Fig. 3(d), the intensities of these features increased greatly and additional lines in this group appeared after IR irradiation.

Upon IR irradiation, intense lines due to HCl at 2894.2 and 2892.1 cm^{-1} increased substantially.[34,35] Weaker lines indicated as group D in Fig. 3(d) and listed in Table V appeared. These features are clearly due to chloroethane (C_2H_5Cl) because the observed line positions are similar to those of the gaseous C_2H_5Cl.[52] We observed in Fig. 3(d) also small proportions of C_2H_5 radicals (group F),[50] a C_2H_4-HCl complex (group C_1),[53,54] and C_2H_6 (group E), as listed in Table V.[55]

2. Experiments with the $Cl_2/^{13}C_2H_2/p$-H_2 matrix

In a few experiments, $^{12}C_2H_2$ was replaced with $^{13}C_2H_2$ and the $Cl_2/^{13}C_2H_2/p$-H_2 matrices were irradiated at 365 nm followed by IR irradiation at 3870–4980 cm^{-1}. A difference spectrum obtained on subtracting the spectrum of the

TABLE III. Comparison of experimental wavenumbers (cm^{-1}) and relative IR intensities of group X ($\cdot$CHClCH$_3$ and $\cdot$^{13}CHCl^{13}CH$_3$) in solid p-H$_2$ with harmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ methods.

				^{13}C-shift	
No.	B3LYP/aug-cc-pVDZ	MP2/aug-cc-pVDZ	p-H$_2$	B3LYP	Expt.
		$\cdot$CHClCH$_3$			
ν_1	3224.3 (12)[a]	3254.6 (18)	3100.8? (18)		
ν_2	3105.0 (29)	3168.2 (20)	2970.2?[b]		
ν_3	3051.6 (34)	3124.5 (25)	2902.3? (22)		
ν_4	2977.3 (54)	3034.9 (38)	2861.2 (27)		
ν_5	1449.1 (7)	1470.1 (8)	1442.6 (5)		
ν_6	1426.8 (20)	1454.9 (23)	1426.6 (23)		
ν_7	1381.7 (17)	1393.5 (20)	1377.1 (25)		
ν_8	1283.4 (100)	1304.7 (100)	1283.4 (100)		
ν_9	1114.5 (12)	1133.2 (10)	1106.0? (6)		
ν_{10}	1025.0 (44)	1037.0 (45)	1027.6 (61)		
ν_{11}	980.7 (0)	997.8 (0)			
ν_{12}	719.5 (71)	744.5 (68)	738.2 (>50)[b]		
ν_{13}	360.8 (22)	472.9 (65)			
ν_{14}	285.3 (54)	336.1 (5)			
ν_{15}	142.0 (5)	182.4 (0)			
		$\cdot$^{13}CHCl^{13}CH$_3$			
ν_1	3213.6 (11)	3244.2 (17)	3091.0? (11)	− 10.7	− 9.8
ν_2	3093.8 (33)	3156.8 (22)	2958.6? (21)	− 11.2	− 11.6
ν_3	3042.7 (36)	3114.6 (29)	2889.5?[b]	− 8.9	− 12.8
ν_4	2971.4 (61)	3030.5 (43)	2857.4 (34)	− 5.9	− 3.8
ν_5	1447.4 (8)	1468.4 (9)	1441.4?[b]	− 1.7	− 1.3
ν_6	1424.6 (22)	1452.6 (26)	1424.1 (27)	− 2.2	− 2.5
ν_7	1370.0 (14)	1379.9 (17)	1366.4 (36)	− 11.7	− 10.7
ν_8	1272.0 (100)	1293.1 (100)	1272.3 (100)	− 11.4	− 11.1
ν_9	1083.2 (14)	1102.1 (14)	1064.0? (8)	− 31.3	− 42.0
ν_{10}	1010.6 (56)	1022.9 (54)	1012.9 (95)	− 14.4	− 14.7
ν_{11}	971.3 (3)	987.2 (0)		− 9.4	
ν_{12}	703.9 (81)	729.1 (74)	723.2 (52)	− 15.6	− 15.0
			718.1 (29)		− 20.1
ν_{13}	355.8 (28)	468.4 (74)		− 5.0	
ν_{14}	283.8 (58)	329.5 (6)		− 1.5	
ν_{15}	143.6 (6)	181.8 (0)		+1.6	

[a] Relative IR intensities normalized to the most intense line. Intensities of lines near 1283 cm^{-1} for CHClCH$_3$ are 41 (B3LYP) and 40 (MP2) km mol^{-1}. Those near 1272 cm^{-1} for ^{13}CHCl^{13}CH$_3$ are 36 (B3LYP) and 35 (MP2) km mol^{-1}, respectively.

[b] The intensity is difficult to determine because of severe overlap with other lines.

Cl$_2$/^{13}C$_2$H$_2$/p-H$_2$ (1/1.3/4000) matrix, deposited at 3.2 K for 8.5 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 4(a). A similar spectrum obtained on subtracting the spectrum of the Cl$_2$/^{13}C$_2$H$_2$/p-H$_2$ (1/1/2000) matrix, deposited at 3.2 K for 7 h, from the spectrum recorded after irradiation at 365 nm for 3 h is presented in Fig. 4(b).

Lines in group A, assigned to ^{13}C$_2$H$_3$Cl, were identified at 3073.9, 1561.7, 1356.8, 1274.9, 1016.9, 941.1, 886.9, 703.0, 697.5, and 612.6 cm^{-1}, as listed in Table V and marked as "A" in Fig. 4(a). The largest isotopic shift was observed for the C = C stretching mode with a shift of 48.1 cm^{-1} and an isotopic ratio of 1561.7/1609.8 = 0.9701, in agreement with values 55.1 cm^{-1} and 1608.2/1663.3 = 0.9669 according to harmonic vibrational wavenumbers predicted with the B3LYP method. A comparison of vibrational wavenumbers observed for C$_2$H$_3$Cl and ^{13}C$_2$H$_3$Cl and the harmonic vibrational wavenumbers predicted with B3LYP is listed in Table S2, see supplementary material.[46]

Lines in group X were observed at 2857.4, 1424.1, 1366.4, 1272.3, 1012.9, 723.2, and 718.1 cm^{-1}, as listed in Table III and marked as "X" in Fig. 4(a). Weak lines at 3091.0, 2958.6, 2889.5, 1441.4, and 1064.0 cm^{-1} might also belong to group X and are marked as "X?" in Fig. 4(a). The line at 723.2 cm^{-1}, shifted from 738.2 cm^{-1} of the ^{12}C-species, possesses the largest isotopic shift, with an isotopic ratio of 723.2/738.2 = 0.9797.

Vibrational wavenumbers of other minor lines of known species observed in the Cl$_2$/^{13}C$_2$H$_2$/p-H$_2$ experiments are listed in Table V.

TABLE IV. Comparison of harmonic vibrational wavenumbers (in cm^{-1}) and IR intensities of three conformers of $\cdot$CDClCH$_2$D predicted with the B3LYP/aug-cc-pVDZ method with experimental wavenumbers and relative intensities in solid p-H$_2$.

Mode	*syn*-CDClCH$_2$D	*anticlinal*-CDClCH$_2$D	*anti*-CDClCH$_2$D	p-H$_2$
ν_1	3062.2 (40)[a]	3093.3 (23)	3103.9 (24)	
ν_2	2985.6 (69)	2983.5 (38)	3042.8 (25)	
ν_3	2377.1 (10)	2376.8 (5)	2376.8 (6)	
ν_4	2262.3 (18)	2240.1 (11)	2186.2 (22)	
ν_5	1425.4 (20)	1415.5 (9)	1419.3 (13)	1418.2 (26)
ν_6	1289.0 (53)	1285.0 (11)	1286.8 (8)	1286.1 (10)
ν_7	1245.5 (13)	1263.8 (5)	1278.0 (11)	1246.6 (7)
ν_8	1128.6 (100)	1148.4 (100)	1139.4 (100)	1121.4 (100)
ν_9	1011.9 (70)	1004.9 (9)	1038.2 (17)	1045.8 (~8)[b]
ν_{10}	929.4 (17)	870.7 (1)	847.9 (1)	915.2 (5)
ν_{11}	810.5 (20)	821.5 (1)	807.3 (1)	816.8 (14)
				814.8 (5)
ν_{12}	657.0 (57)	701.7 (47)	706.2 (52)	668.5 (30)
				665.4 (13)
ν_{13}	339.4 (10)	328.4 (4)	342.5 (6)	
ν_{14}	245.8 (50)	250.5 (26)	241.5 (26)	
ν_{15}	121.3 (7)	122.0 (3)	121.2 (4)	

[a] Relative IR intensities normalized to the most intense line. Intensities of lines near 1283 cm^{-1} for *syn*-, *anticlinal*-, and *anti*-CDClCH$_2$D are 30.5, 58.1, and 52.6 km mol^{-1}, respectively.

[b] The intensity is difficult to determine because of severe overlap with the line of C$_2$H$_2$.

3. Experiments with the Cl$_2$/C$_2$D$_2$/p-H$_2$ matrix

We performed a few experiments with C$_2$D$_2$ replacing C$_2$H$_2$. The difference spectra obtained after irradiation at 365 nm of the Cl$_2$/C$_2$D$_2$/p-H$_2$ (1.5/1.0/3000) matrix and after further irradiation in the 3870−4980 cm^{-1} region are shown in Figs. 5(a) and 5(b), respectively.

Lines in group A shifted to 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm^{-1} (group A$_t$ in Table V and Fig. 5(a)). Possible deuterated isomers of chloroethene produced from Cl + C$_2$D$_2$ are *trans*-CHDCDCl and *cis*-CHDCDCl, in which the *trans*- and *cis*-conformations refer to the relative position of D atoms. Comparison of line positions and relative IR intensities of *trans*-CHDCDCl, *cis*-CHDCDCl, and CHClCD$_2$ with experimental observations is available from Table S3 in the supplementary material.[46] Lines in group A matches better with those predicted for *trans*-CHDCDCl, to be discussed in Sec. IV B 2.

The lines in group X shifted to 1418.2, 1286.1, 1246.6, 1121.4, 1045.8, 915.2, 816.8, 814.8, 668.5, and 665.4 cm^{-1}, as listed in Table IV. They are assigned to $\cdot$CDClCH$_2$D, to be discussed in Sec. IV B.

As a result of secondary IR irradiation of the 365-nm irradiated Cl$_2$/C$_2$D$_2$/p-H$_2$ matrix, lines due to the formation of minor products *cis*-CHDCDCl (group A$_c$), *syn*-CH$_2$DCHDCl (group D$_a$), *anti*-CH$_2$DCHDCl (group D$_b$), *cis*-CHDCHD (group C$_c$), *trans*-CHDCHD (group C$_t$), *trans*-CHDCHD-HCl complex (group C$_{1t}$), and C$_2$H$_3$D (group C$_H$) were observed, as indicated in Fig. 5(b) with observed wavenumbers listed in Table V. A comparison with calculated vibrational wavenumbers and IR intensities of these products is listed in Table S4, available from the supplementary material.[46]

IV. DISCUSSION

A. Assignments of lines in group X observed in the Cl$_2$/C$_2$H$_2$/p-H$_2$ and Cl$_2$/^{13}C$_2$H$_2$/p-H$_2$ experiments to the 1-chloroethyl ($\cdot$CHClCH$_3$) radical

The expected carrier of the new lines in group X is the product of the Cl + C$_2$H$_2$ addition reaction, *cis*- or *trans*-CHCHCl, or their secondary reaction products, but observed line positions and relative IR intensities do not match with those predicted for *cis*- and *trans*-CHCHCl, as listed in Table II. The intense IR lines of *trans*-CHCHCl are predicted at 1637, 826, 783, and 639 cm^{-1}, and those of *cis*-CHCHCl are at 1635, 821, 618, and 578 cm^{-1}, both inconsistent with our observation. These features of group X can neither be ascribed to the products of a H-abstraction channel, the ethynyl radical (C$_2$H) or the C$_2$H-HCl complex. Vibrational wavenumbers of C$_2$H isolated in a Ne matrix are reported to be 3293.3 and 1835.5 cm^{-1},[56–58] inconsistent with our observation.

From Fig. 3(d), we observed that lines in group X diminished upon secondary IR irradiation, whereas those of C$_2$H$_5$Cl increased. We reasonably assume that, upon secondary IR irradiation of the matrix, this species reacts with H or H$_2$ to form C$_2$H$_5$Cl. The most likely candidate for this unstable carrier of lines in group X is thus the C$_2$H$_4$Cl radical. Two isomers of C$_2$H$_4$Cl are stable: 1-chloroethyl ($\cdot$CHClCH$_3$) and 2-chloroethyl ($\cdot$CH$_2$CH$_2$Cl) radicals. These radicals are expected to react readily with H or H$_2$ to form C$_2$H$_5$Cl upon irradiation of the p-H$_2$ matrix with IR light.

Our group reported the infrared spectra of 2-chloroethyl radicals observed upon irradiation at 365 nm of a matrix containing Cl$_2$ and C$_2$H$_4$;[29] lines at 3129.3, 3041.1, 1228.0, 1069.9, 664.0, and 562.1 cm^{-1} are assigned to $\cdot$CH$_2$CH$_2$Cl, with the line at 664.0 cm^{-1} being the most intense. Observed lines in group X do not match with those of the 2-chloroethyl radical.

The three most intense IR lines under 2000 cm^{-1} predicted for the 1-chloroethyl ($\cdot$CHClCH$_3$) radical with the B3LYP method are at 1283, 1025, and 720 cm^{-1} (Table III). They are assigned to the CCH bending, CH$_3$ rocking, and C−Cl stretching modes, respectively. These values fit satisfactorily with the three most intense lines at 1283.4, 1027.6, and 738.2 cm^{-1} observed in group X, as shown in Figs. 3(a) and 3(b). Other lines of group X at 2861.2, 1442.6, 1426.6, and 1377.1 cm^{-1} also fit with lines predicted near 2977, 1449, 1427, and 1382 cm^{-1} with acceptable relative intensities. Weak lines at 3100.8, 2970.2, 2902.3, and 1106.0 cm^{-1} might be associated also with group X; the wavenumbers are consistent with harmonic vibrational wavenumbers predicted near 3224, 3105, 3052, and 1115 cm^{-1}, as compared in Table III.

For the ^{13}C-substituted species, these three most intense lines shift to 1272.3 cm^{-1} (shift $\Delta = -11.1$), 1012.9 cm^{-1} ($\Delta = -14.7$), and 723.2 cm^{-1} ($\Delta = -15.0$ cm^{-1}), respec-

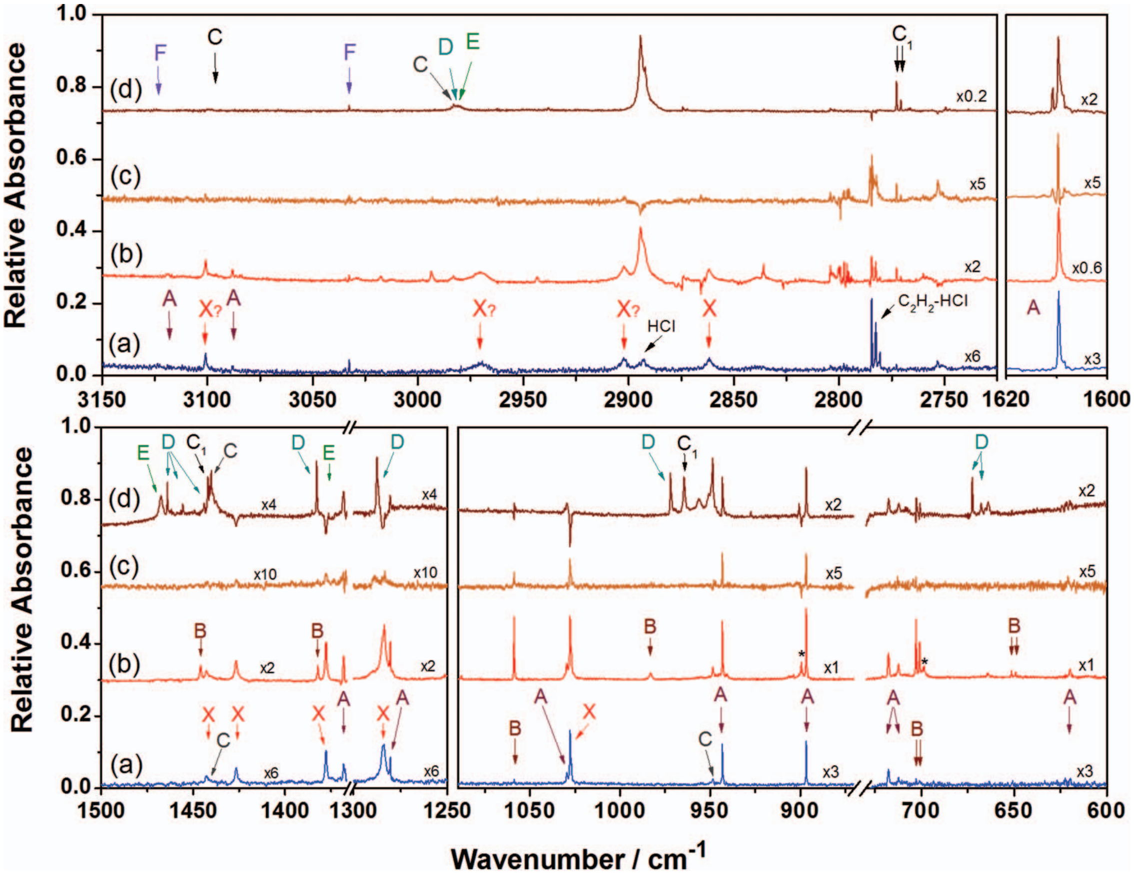

FIG. 3. (a) Difference spectrum of a $Cl_2/C_2H_2/p$-H_2 (1/2/6000) matrix, deposited for 7 h at 3.2 K, after irradiation at 365 nm for 5 h. (b) Difference spectra of a $Cl_2/C_2H_2/p$-H_2 (1/1/2000) matrix, deposited for 5 h and annealed at 4.3 K for 0.5 h, after irradiation at 365 nm for 3 h; (c) after annealing at 4.3 K for 0.5 h; (d) after further irradiation with light in the range 3870−4970 cm^{-1} with a globar for 4 h. All spectra were recorded at 3.2 K with resolution 0.25 cm^{-1}. The assignments of lines in each group are A: C_2H_3Cl, B: $CHCl_2CH_3$, C: C_2H_4, C_1: C_2H_4-HCl complex, D: C_2H_5Cl, E: C_2H_6, F: C_2H_5, and X: $\cdot CHClCH_3$.

tively, as shown in Figs. 4(a) and 4(b). These isotopic shifts agree with predicted values of −11.4, −14.4, and −15.6 cm^{-1}, as compared in Table III. For lines at 2861.2, 1426.6, and 1377.1 cm^{-1}, the ^{13}C-isotopic shifts are −3.8, −2.5, and −10.7 cm^{-1}, consistent with predicted values of −5.9, −2.2, and −11.7 cm^{-1}, respectively. Although the deviation between observed and predicted isotopic shifts for the line at 2861.2 cm^{-1} seems slightly larger than for other lines, the corresponding isotopic ratios of 0.9987 and 0.9980 are similar. The larger discrepancy in the isotopic shift is mainly due to the large anharmonicity for the C−H stretching mode that results in a large deviation in observed vibrational wavenumbers and predicted harmonic vibrational wavenumbers.

Based on the photolytic behavior, comparison of observed and predicted vibrational wavenumbers, relative IR intensities, and ^{13}C-isotpic shifts, we assigned lines in group X to the 1-chloroethyl ($\cdot CHClCH_3$) radical.

B. Assignments of observed lines in the $Cl_2/C_2D_2/p$-H_2 experiment

1. The assignment of lines in group X to *syn*-$CDClCH_2D$

When C_2H_2 is replaced with C_2D_2, we expect that $\cdot CDClCH_2D$ or $\cdot CHDCHDCl$ to be formed if both additional hydrogen atoms come from the *p*-H_2 matrix host. Because the 2-chloroethyl ($\cdot CH_2CH_2Cl$) radical has been excluded as the possible carrier for lines in group X, as discussed in Sec. IV A, the most likely carrier of these features in this experiment is $\cdot CDClCH_2D$. As a further proof, the predicted IR lines for conformers of $\cdot CHDCHDCl$, listed in Table S1 in the supplementary material,[46] fail to match with our experimental observations of lines in group X.

Figure 5 compares the lines in group X observed in the $Cl_2/C_2D_2/p$-H_2 experiments (trace a) with the simulated IR spectra (traces c−e) for the three conformers of $\cdot CDClCH_2D$. Although we are unable to exclude positively the contribution of a specific conformer, observed lines of group X in these experiments fit best with those predicted for *syn*-$CDClCH_2D$, as shown in Fig. 5(c) and compared in Table IV. The line observed at 816.8 cm^{-1} with an intensity ∼14% of the most intense feature at 1121.4 cm^{-1} fits with one predicted at 811 cm^{-1} that has an intensity ∼20% that of the most intense line predicted at 1129 cm^{-1} for *syn*-$CDClCH_2D$, whereas the corresponding lines of *anticlinal*-$CDClCH_2D$ and *anti*-$CDClCH_2D$ at 822 and 807 cm^{-1} are predicted to have <1% intensity of the most intense feature. The separation of observed lines at 1286.1 and 1246.6 cm^{-1} (39.5 cm^{-1}) also fit better with that predicted for *syn*-$CDClCH_2D$ (43.5 cm^{-1}) than those of *anticlinal*-$CDClCH_2D$ (31.2 cm^{-1}) and *anti*-$CDClCH_2D$ (8.8 cm^{-1}). Furthermore, the observed line at 915.2 cm^{-1} fits much better with a line predicted for *syn*-$CDClCH_2D$ at 929 cm^{-1} than

TABLE V. Observed wavenumbers and relative IR intensities for lines of various groups ascribable to known species.

Group	Species	Observed wavenumbers (cm^{-1}) and relative intensities[a]
	$Cl_2/C_2H_2/p$-H_2 matrix	
A	C_2H_3Cl	3118.7 (2), 3088.1 (5), 1609.8 (100), 1368.1 (9), 1280.3 (15), 1029.4 (18), 943.2 (41), 896.5 (45), 717.6 (26), 712.6 (20), 619.8 (14)
B	$CHCl_2CH_3$	1445.8 (40), 1382.1 (26), 1232.3 (41), 1088.1 (9), 1058.7 (94), 983.1 (31), 702.8 (100), 700.9 (67), 651.3 (9), 649.1 (8)
C	C_2H_4	3097.8, 2984.5, 1440.0 (13), 948.4 (100)
C_1	C_2H_4-HCl	2772.6, 2770.6 (428), 1441.9 (12), 964.3 (100)
D	C_2H_5Cl	2982.9 (40), 1464.0 (32), 1455.7 (6), 1444.0 (11), 1382.7 (42), 1287.5 (87), 972.0 (100), 784.9 (14), 672.5 (79), 667.7 (34)
E	C_2H_6	2981.3 (100); 1467.5 (12); 1376.3 (2); 820.9, 822.0, 824.3 (10)
F	C_2H_5	3123.3 (?), 3032.6 (19), 538.0 (100)
	$Cl_2/^{13}C_2H_2/p$-H_2 matrix	
A	$^{13}C_2H_3Cl$	3073.9(6), 1561.7 (100), 1356.8 (20), 1274.9 (18), 1016.9 (38), 941.1 (66), 886.9 (59), 703.0 (34), 697.5 (24), 612.6 (17)
B	$^{13}CHCl_2{}^{13}CH_3$	1441.3 (57), 1373.0 (27), 1222.2 (25), 1060.8 (7), 1045.5 (96), 965.3 (27), 685.2 (100), 683.4 (69), 636.8 (10), 634.7 (9)
C	$^{13}C_2H_4$	3087.9 (24), 2974.8, 1434.3 (23), 943.5 (100)
C_1	$^{13}C_2H_4$-HCl	2772.6, 2770.5 (424), 1435.1(15), 959.3(100)
D	$^{13}C_2H_5Cl$	2972.7, 2932.2 (17), 1461.1 (10), 1451.8 (7), 1441.8, 1372.0 (13), 1286.6 (19), 952.0 (100), 782.2 (1), 657.5 (20), 651.8 (22)
E	$^{13}C_2H_6$	2971.1 (100), 1463.0 (8), 1367.3 (1), 819.2, 820.8, 823.2 (8)
F	$^{13}C_2H_5$	3110.6?, 3026.5 (26), 534.7 (100)
	$Cl_2/C_2D_2/p$-H_2 matrix	
A_t	*trans*-CHDCDCl	1560.6 (100), 1268.1 (18), 993.9 (38), 851.5 (36), 697.6 (47), 692.0 (86)
A_c	*cis*- CHDCDCl	1562.4 (100), 1032.5 (20), 867.0 (74), 821.7(8), 664.5 (33)
C_t	*trans*-CHDCHD	1295.8 (24), 986.0 (100), 724.9 (62)
C_c	*cis*-CHDCHD	1338.9 (15), 841.7 (100)
C_H	C_2H_3D	1398.8 (17), 942.2 (100), 805.9 (39)
C_{1t}	*trans*-CHDCHD-HCl	2771.2 (188), 2769.1 (100), 996.7 (100), 743.6 (82)
D_a	*syn*-$CH_2DCHDCl$	1428.5 (64), 1329.0 (17), 1298.8 (15), 1240.6 (25), 1092.9 (100), 1011.4 (50)?, 926.6 (40), 792.3 (35), 626.8 (40)
D_b	*anti*-$CH_2DCHDCl$	1416.2 (62), 1322.5 (22), 1288.3 (16), 1280.9 (15), 1232.4 (37), 1091.4 (23), 992.7 (100), 675.7 (13), 660.9 (23)

[a] Percentage IR intensities relative to the most intense line of the species are listed in parentheses.

those for *anticlinal*-$CDClCH_2D$ (1005 or 871 cm^{-1}) and *anti*-$CDClCH_2D$ (1038 or 848 cm^{-1}).

Considering the photochemical behavior and comparison of the spectral pattern of experimentally observed lines with that predicted for various isomers of isotopically substituted chloroethyl radicals, we conclude that lines in group X are due to 1-chloroethyl ($\cdot CHClCH_3$) radical that was not previously identified experimentally. In contrast, when Cl was added to C_2H_4, only the 2-chloroethyl ($\cdot CH_2CH_2Cl$) radical was observed.[29] In the experiments with $Cl_2/C_2D_2/p$-H_2, 1-chloroethyl radical $\cdot CDClCH_2D$ is formed and the most likely configuration is *syn*-$CDClCH_2D$.

2. The assignment of lines in group A to trans-CHDCDCl

Lines in group A observed in the $Cl_2/C_2H_2/p$-H_2 experiments are due to C_2H_3Cl, as discussed in Sec. III C. In the experiment with $Cl_2/C_2D_2/p$-H_2, we expect that CHDCDCl molecules are formed. This species has two stable

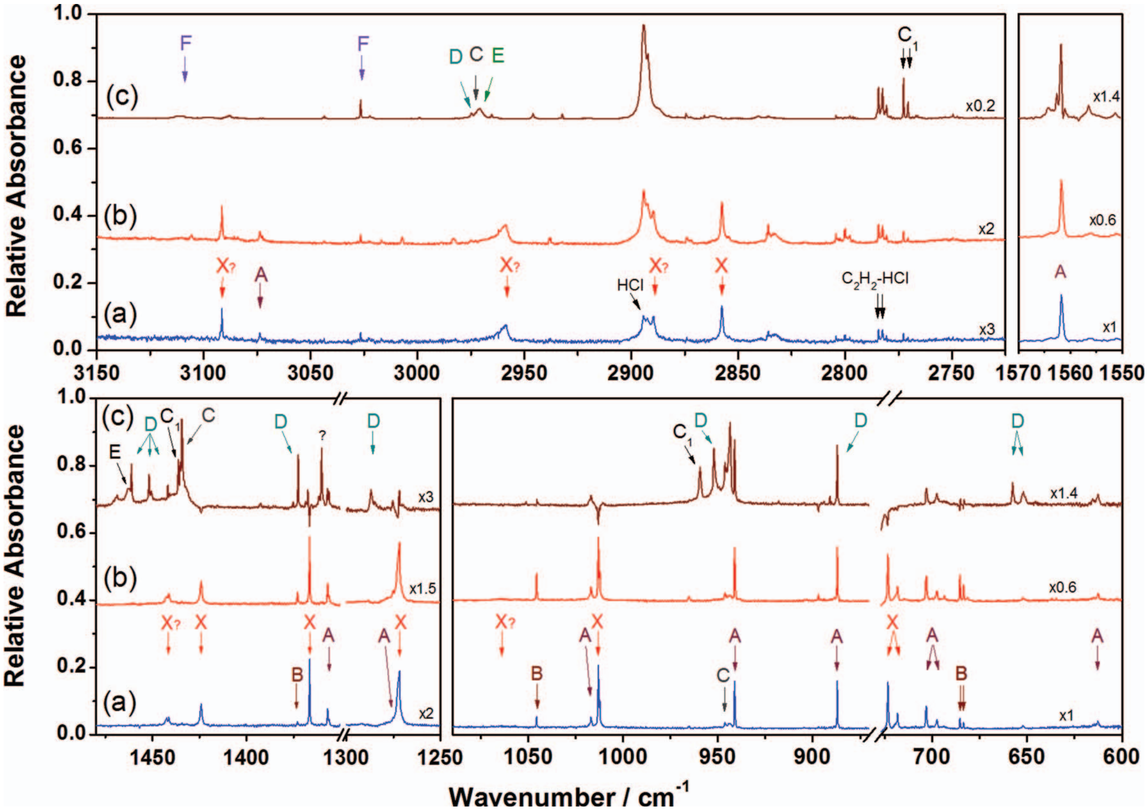

FIG. 4. (a) Difference spectrum of a $Cl_2/^{13}C_2H_2/p\text{-}H_2$ (1/1.3/4000) matrix, deposited for 8.5 h at 3.2 K, after irradiation at 365 nm for 3 h. (b) Difference spectra of a $Cl_2/^{13}C_2H_2/p\text{-}H_2$ (1/1/2000) matrix, deposited for 7 h at 3.2 K, after irradiation at 365 nm for 3 h; (c) after further irradiation with light in the range 3870−4970 cm^{-1} from a globar lamp for 4 h. All spectra were recorded at 3.2 K with resolution 0.25 cm^{-1}. The assignments of lines in each group are A: $^{13}C_2H_3Cl$, B: $^{13}CHCl_2{}^{13}CH_3$, C: $^{13}C_2H_4$, C_1: $^{13}C_2H_4$-HCl complex, D: $^{13}C_2H_5Cl$, E: $^{13}C_2H_6$, F: $^{13}C_2H_5$, and X: $\cdot{}^{13}CHCl^{13}CH_3$.

isomers: *trans*-CHDCDCl and *cis*-CHDCDCl. The predicted harmonic vibrational wavenumbers of *trans*-CHDCDCl, *cis*-CHDCDCl, and $CHClCD_2$ are listed in Table S3 of the supplementary material.[46]

Figure 5 shows a comparison of observed lines in group A_t (trace a) with calculated stick spectra for *trans*-CHDCDCl (trace f) and *cis*-CHDCDCl (trace g). The predicted spectrum of *trans*-CHDCDCl clearly fits better with the experimentally observed spectrum of group A_t in the $Cl_2/C_2D_2/p\text{-}H_2$ experiment in terms of line positions and relative IR intensities. The six intense features of *trans*-CHDCDCl are predicted to be 1611, 1275, 997, 882, 705, and 683 cm^{-1}, whereas the corresponding lines of *cis*-CHDCDCl are predicted to be 1615, 1268, 1033, 898, and 652 cm^{-1}. Observed lines at 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm^{-1} (Table V) fit better with those predicted for *trans*-CHDCDCl. The experimentally observed deuterium isotopic ratios of 0.9694, 0.9269, 0.7763, 0.9498, 0.7396, and 0.9643 for lines at 1560.6, 1268.1, 993.9, 851.5, 697.6, and 692.0 cm^{-1}, respectively, are in satisfactory agreement with the values 0.9683, 0.9162, 0.7734, 0.9430, 0.7326, and 0.9720 predicted with B3LYP calculations (Table S3 of the supplementary material).[46]

As further support, we identified lines at 1562.4, 1032.5, 867.0, 821.7 (weak), and 664.5 cm^{-1} as group A_c (Fig. 5(b)) upon secondary IR irradiation of the 365-nm irradiated $Cl_2/C_2D_2/p\text{-}H_2$ matrix. These lines might be assigned to *cis*-CHDCDCl according to comparison with harmonic vibrational wavenumbers and IR intensities predicted with quantum-chemical calculations. We conclude hence that lines in group A_t observed in the experiments with $Cl_2/C_2D_2/p\text{-}H_2$ are due to *trans*-CHDCDCl.

C. Reaction mechanisms in $p\text{-}H_2$

1. Formation of C_2H_3Cl and $\cdot CHClCH_3$ from $Cl_2/C_2H_2/p\text{-}H_2$ experiments

The abstraction channel of the Cl + C_2H_2 reaction has a barrier of 123−139 kJ mol^{-1},[15] inaccessible under our experimental conditions; consequently no line ascribable to C_2H was observed. According to computations with the CCSD(T) or G3 method,[15] the addition channel to form a C_2H_2-Cl complex, 11−17 kJ mol^{-1} more stable than Cl + C_2H_2, is barrierless and the C_2H_2-Cl complex has a small barrier of ∼2 kJ mol^{-1} for conversion to *trans*-CHCHCl (chlorovinyl) radicals, which are the originally expected product for the reaction of Cl + C_2H_2 in solid *p*-H_2 at low temperature. The energies of *trans*-CHCHCl are predicted to be 57−73 kJ mol^{-1} smaller than Cl + C_2H_2. The barrier for isomerization of *trans*-CHCHCl to *cis*-CHCHCl is predicted to be ∼21 kJ mol^{-1}. The energy of *cis*-CHCHCl exceeds that of *trans*-CHCHCl by 4−5 kJ mol^{-1}.[1,15]

In this experiment, we observed C_2H_3Cl and $\cdot CHClCH_3$ as the major products but no IR absorption ascribable to *trans*-CHCHCl or *cis*-CHCHCl or the C_2H_2-Cl complex.

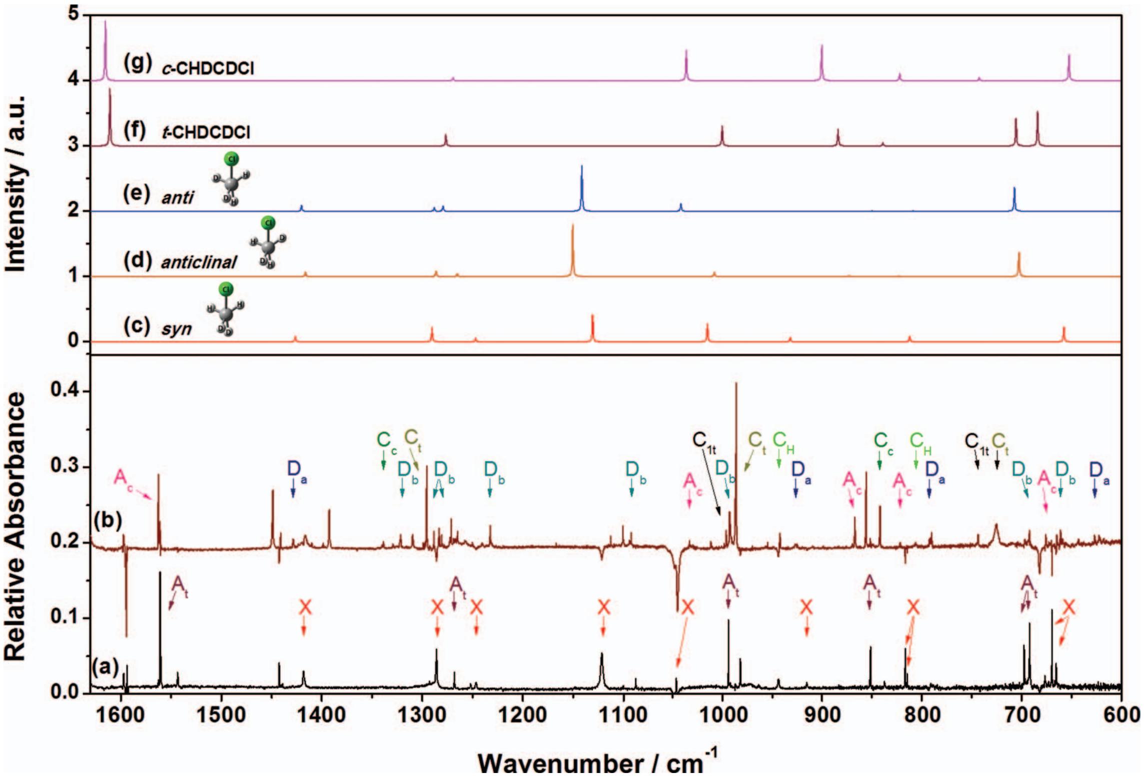

FIG. 5. (a) Difference spectra of a $Cl_2/C_2D_2/p$-H_2 (1.5/1/3000) matrix, deposited for 7 h at 3.2 K, after irradiation at 365 nm for 3 h; (b) after irradiation with light in the range 3870−4970 cm^{-1} from a globar lamp for 4 h. In this experiment the matrix was annealed to 4.3 K for 15 min before IR irradiation. All spectra were recorded at 3.2 K with resolution 0.25 cm^{-1}. IR spectra simulated according to predicted harmonic vibrational wavenumbers and IR intensities for *syn*-$CDClCH_2D$ (c), *anticlinal*-$CDClCH_2D$ (d), *anti*-$CDClCH_2D$ (e), *trans*-CHDCDCl (f), and *cis*-CHDCDCl (g); spectral widths of 0.5 cm^{-1} were applied. The assignments of lines in each group are A_t: *trans*-CHDCDCl, A_c: *cis*-CHDCDCl, C_t: *trans*-CHDCHD, C_c: *cis*-CHDCHD, C_H: $CHDCH_2$, C_{1t}: *trans*-CHDCHD-HCl complex, D_a: *syn*-$CH_2DCHDCl$, D_b: *anti*-$CH_2DCHDCl$, X: *syn*-$CDClCH_2D$.

These results indicate that the originally expected primary products, *trans*-CHCHCl and/or *cis*-CHCHCl, might react readily with a neighboring p-H_2 molecule to form C_2H_3Cl and $\cdot CHClCH_3$. This assumption is supported by the results of experiments with the $Cl_2/C_2D_2/p$-H_2 matrix, in which *trans*-CHDCDCl and $\cdot CDClCH_2D$ were formed, indicating that the extra H atoms come from the matrix host, not from the reactant C_2D_2. The most likely processes for the reaction of $\cdot$CHCHCl are thus

$$\cdot CHCHCl + H_2 \rightarrow C_2H_3Cl + H \tag{1}$$

$$C_2H_3Cl + H \rightarrow \cdot CHClCH_3 \text{ (1-chloroethyl)} \tag{2a}$$

$$\rightarrow \cdot CH_2CH_2Cl \text{ (2-chloroethyl)}. \tag{2b}$$

The H atom produced in reaction (1) might also react with CHCHCl to form C_2H_3Cl,

$$\cdot CHCHCl + H \rightarrow C_2H_3Cl. \tag{3}$$

The enthalpy change of reaction (1) is about −6 kJ mol^{-1} if we compare the bond energy of H_2 (436 kJ mol^{-1}) and the enthalpy change of −442 kJ mol^{-1} for reaction (3) predicted with the QCISD(T)/6-311+G(d,p) method.[59]

Mebel *et al*. investigated a similar system $C_2H_3 + H_2$ using UMP2/6-311G(d,p) and QCISD/6-311G(d,p) methods and concluded that direct 1,1- or 1,2-insertion of H_2 to C_2H_3 to form C_2H_5 does not occur. The reaction proceeds with a barrier of height 44 kJ mol^{-1} to form C_2H_4 + H, followed by a second barrier of height 20 kJ mol^{-1} to form C_2H_5, which has energy 169 kJ mol^{-1} smaller than that of $C_2H_3 + H_2$.[60] The reaction channels of the reaction $C_2H_3 + H_2 \rightarrow C_2H_4 + H \rightarrow C_2H_5$ are similar to those of reactions (1) and (2).

We performed similar calculations on the $\cdot$CHCHCl + H_2 system using the G2//MP2/6-311++G(d, p) method and found a similar trend, as shown in Fig. 6. Reaction (1) proceeds with a barrier of height 32 kJ mol^{-1} to form C_2H_3Cl + H. Reaction (2a) is followed by a second barrier of height 10 kJ mol^{-1} to form $\cdot CHClCH_3$, which has energy 194 kJ mol^{-1} lower than that of $\cdot$CHCHCl + H_2. Reaction (2b) has a barrier of height 24 kJ mol^{-1} to form $\cdot CH_2CH_2Cl$, which has energy 177 kJ mol^{-1} lower than that of $\cdot$CHCHCl + H_2. According to calculations using the QCISD(T)/aug-cc-pVDZ method, the energy of 1-chloroethyl is ∼10 kJ mol^{-1} less than that of 2-chloroethyl,[45] our calculated value of 17 kJ mol^{-1} is consistent with this result. Reaction (2) was also investigated by Barat and Bozzelli using the quantum Rice-Ramsperger-Kassel (QRRK) method. An activation energy of 12 kJ mol^{-1} and exothermicity of 169 kJ mol^{-1} were derived for reaction (2a), whereas an activation energy of 24 kJ mol^{-1} and exothermicity of 152 kJ mol^{-1}

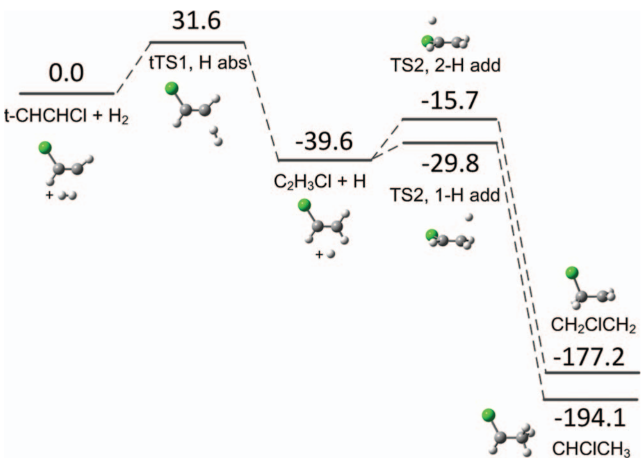

FIG. 6. Potential-energy profile for the reaction *trans*-CHCHCl + H_2 to form C_2H_3Cl + H and, subsequently, 1-chloroethyl ($\cdot$ $CHClCH_3$) and 2-chloroethyl ($\cdot$ CH_2CH_2Cl) radicals. ZPE-corrected energies in kJ mol^{-1} were predicted with the G2//MP2/6-311G++(d,p) method.

were derived for reaction (2b).[61] Our calculated barriers agree with their values.

Although reaction (1) has a barrier of height 32 kJ mol^{-1}, similar to that of $C_2H_3 + H_2$, the exothermicity of the reaction,

$$Cl + C_2H_2 \rightarrow C_2H_2Cl, \tag{4}$$

predicted to be ~70 kJ mol^{-1}, is much larger than the barrier of reaction (1). Reaction (1) might hence proceed through the transition state to form C_2H_3Cl and H, and subsequently $\cdot CHClCH_3$. For this reason, we observed C_2H_3Cl and $\cdot CHClCH_3$ as the major products upon irradiation of the $Cl_2/C_2H_2/p$-H_2 matrix at 365 nm.

In these experiments, only $\cdot CHClCH_3$ (1-chloroethyl), not $\cdot CH_2CH_2Cl$ (2-chloroethyl) radical, was observed as a major product. The reason might be that the H atom produced in reaction (1) is near the C atom attacked by the first H atom, rather than the C atom bound to the Cl atom. Reaction (2a) is hence much more facile than reaction (2b). That the activation energy predicted for reaction (2b) is much larger than that for reaction (2a) might also play an important role.[61] The barrier height for the interconversion between 1- and 2-chloroethyl radicals is about 167 kJ mol^{-1}, too large to overcome under our experimental conditions.[45,61]

2. Formation of trans-CHDCDCl and $\cdot CDClCH_2D$ from the $Cl_2/C_2D_2/p$-H_2 experiments

According to a similar mechanism, for reactions involving Cl + C_2D_2, we expect to observe CHDCDCl from reaction (5) and $\cdot CDClCH_2D$ from reaction (6a)

$$\cdot CDCDCl + H_2 \rightarrow CHDCDCl + H, \tag{5}$$

$$CHDCDCl + H \rightarrow \cdot CDClCH_2D\,(\text{1-chloroethyl}) \tag{6a}$$

$$\rightarrow \cdot CHDCHDCl\,(\text{2-chloroethyl}), \tag{6b}$$

consistent with our observation. The observation of only *trans*-CHDCDCl, not *cis*-CHDCDCl, might indicate that *trans*-CDCDCl is formed initially but it is so reactive that it reacts with H_2 before it has a chance to isomerize to *cis*-CDCDCl. Production of *syn*-$CDClCH_2D$, the conformer with the lowest energy, is consistent with the expectation that internal rotation around the C−C bond has a small barrier in solid *p*-H_2.

3. Product formation upon secondary IR irradiation

Upon secondary IR irradiation, the H_2 molecule is excited and can react with Cl atoms or other free radicals produced after the 365-nm irradiation of the $Cl_2/C_2H_2/p$-H_2 matrix. The reaction of Cl with excited H_2 produces H atoms and HCl.[36] The H atoms thus produced might react subsequently with other species in the matrix, leading to various products.

In this IR-irradiation experimental step we observed the formation of C_2H_3Cl, C_2H_4, and C_2H_5Cl as major products, and C_2H_5 and C_2H_6 as minor products. The formation of additional amount of C_2H_3Cl might be a result of the reaction of H with C_2H_2 to form C_2H_3, which subsequently reacts with a nearby Cl atom to form C_2H_3Cl. Similarly, C_2H_3 might react with H_2 to form C_2H_4 and C_2H_5, which might react with another H atom to form C_2H_6. The formation of C_2H_5Cl is most likely a result of reaction between $\cdot CHClCH_3$ and H or activated H_2.

In the $Cl_2/C_2D_2/p$-H_2 experiments, the formation of *trans*-CHDCHD, *cis*-CDClCHD, and *syn*- and *anti*-$CHDClCH_2D$ as major products corresponds to products C_2H_4, C_2H_3Cl, and C_2H_5Cl, respectively, from the $Cl_2/C_2H_2/p$-H_2 experiments; *cis*-CHDCHD and *trans*-CDClCHD were observed as minor products. The presence of both *cis* and *trans* conformers indicates that the IR light might induce the interconversion between these two conformers.

V. CONCLUSION

Upon irradiation of matrix samples of $Cl_2/C_2H_2/p$-H_2 at 3.2 K with light at 365 nm, we observed C_2H_3Cl and the $\cdot CHClCH_3$ (1-chloroethyl) radical as two major products. The originally expected products of the Cl + C_2H_2 addition reaction, the chlorovinyl ($\cdot$ CHCHCl) radicals, were unobserved. The assignments of lines at 2861.2, 1442.6, 1426.6, 1377.1, 1283.4, 1027.6, and 738.2 cm^{-1} to $\cdot CHClCH_3$ are based on a consideration of possible reactions and a comparison of observed and quantum-chemically predicted vibrational wavenumbers, relative IR intensities, and their isotopic shifts when $^{13}C_2H_2$ and C_2D_2 replaced C_2H_2.

These observations indicate that the product of the addition reaction of Cl + C_2H_2, $\cdot$ CHCHCl radicals, reacts readily with a neighboring H_2 molecule to form C_2H_3Cl + H, followed by reaction of C_2H_3Cl with the nearby H atom to form 1-chloroethyl ($\cdot CHClCH_3$) radicals. Although the reaction of $\cdot$ CHCHCl + H_2 is predicted to have a barrier of height ~32 kJ mol^{-1}, the exothermicity of the reaction Cl + $C_2H_2 \rightarrow \cdot$ CHCHCl, ~70 kJ mol^{-1}, might overcome this barrier to affect a reaction. This mechanism is further supported by the observation of major products *trans*-CHDCDCl and the $\cdot CDClCH_2D$ radical, likely in the *syn*-conformation, when matrix samples of $Cl_2/C_2D_2/p$-H_2 were irradiated at 365 nm.

When the 365-nm irradiated mixtures of $Cl_2/C_2H_2/$ p-H_2 were subsequently irradiated with IR light, which excited H_2 in the matrix and induced its reaction with Cl to form HCl and H atoms, C_2H_3Cl, C_2H_4, and C_2H_5Cl were observed as major products. Observation of *trans*-CHDCHD, *cis*-CDClCHD, and *syn*- and *anti*-$CHDClCH_2D$ as major products in the IR irradiated matrix samples of $Cl_2/C_2D_2/p$-H_2 further support the proposed mechanism.

Although this work demonstrates one disadvantage of using p-H_2 as a matrix host for spectroscopy of free radicals, as the host might react with highly reactive free radicals even at low temperature, the latter reaction might produce other free radicals—in this experiment, the 1-chloroethyl radical, $\cdot CHClCH_3$—that are difficult to produce using conventional methods.

ACKNOWLEDGMENTS

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[1] S. M. Resende, J. R. Pliego, Jr., and W. B. De Almeida, J. Chem. Soc., Faraday Trans. **94**, 2895 (1998).
[2] H. B. Singh and J. F. Kasting, J. Atmos. Chem. **7**, 261 (1988).
[3] J. C. McConnell and G. S. Henderson, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, NATO ASI Series I: Global Environmental Change Vol. 7, edited by H. Niki and K. H. Becker (Springer-Verlag, Berlin, 1993), p. 89.
[4] C. A. Taatjes, Int. Rev. Phys. Chem. **18**, 419 (1999).
[5] D. Cronn and E. Robinson, Geophys. Res. Lett. **6**, 641, doi:10.1029/GL006i008p00641 (1979).
[6] W. A. Payne, D. F Nava, J. Brunning, and L. J. Stieff, J. Geophys. Res. **91**, 4097, doi:10.1029/JD091iD03p04097 (1986).
[7] M. J. Molina, L. T. Molina, and C. E. Kolb, Annu. Rev. Phys. Chem. **47**, 327 (1996).
[8] E. W. Kaiser and T. J. Wallington, J. Phys. Chem. **100**, 4111 (1996).
[9] T. Zhu and G. Yarwood, J. Phys. Chem. **98**, 5065 (1994).
[10] L. Zhu, W. Chen, W. L. Hase, and E. W. Kaiser, J. Phys. Chem. **97**, 311 (1993).
[11] E. W. Kaiser, Int. J. Chem. Kinet. **24**, 179 (1992).
[12] T. J. Wallington, J. M. Andino, I. M. Lorkovic, W. E. Kaiser, and G. Marston, J. Phys. Chem. **94**, 3644 (1990).
[13] J. Brunning and L. J. Stief, J. Chem. Phys. **83**, 1005 (1985).
[14] F. S. C. Lee and F. S. Rowland, J. Phys. Chem. **81**, 684 (1977).
[15] J.-L. Li, C.-Y. Geng, X.-R. Huang, J.-H. Zhan, and C.-C. Sun, Chem. Phys. **331**, 42 (2006).
[16] H. Tanskanen, L. Khriachtchev, M. Räsänen, V. I. Feldman, F. F. Sukhov, A. Y. Orlov, and D. A. Tyurin, J. Chem. Phys. **123**, 64318 (2005).
[17] I. U. Goldschleger, A. V. Akimov, E. Y. Misochko, and C. A. Wight, J. Mol. Spectrosc. **205**, 269 (2001).
[18] M. E. Jacox, Chem. Phys. **53**, 307 (1980).
[19] Y. A. Tobón, L. I. Nieto, R. M. Romano, C. O. Della Védova, and A. J. Downs, J. Phys. Chem. A **110**, 2674 (2006).
[20] Y. A. Tobón, R. M. Romano, C. O. Della Védova, and A. J. Downs, Inorg. Chem. **46**, 4692 (2007).
[21] T. Oka, Annu. Rev. Phys. Chem. **44**, 299 (1993).
[22] T. Momose and T. Shida, Bull. Chem. Soc. Jpn. **71**, 1 (1998).
[23] T. Yoshioka, P. L. Raston, and D. T. Anderson, Int. Rev. Phys. Chem. **25**, 469 (2006).
[24] Y.-P. Lee, Y.-J. Wu, R. M. Lees, L.-H. Xu, and J. T. Hougen, Science **311**, 365 (2006).
[25] N. Sogoshi, T. Wakabayashi, T. Momose, and T. Shida, J. Phys. Chem. A **101**, 522 (1997).
[26] M. Fushitani, N. Sogoshi, and T. Wakabayashi, J. Chem. Phys. **109**, 6346 (1998).
[27] M. Bahou and Y.-P. Lee, J. Chem. Phys. **133**, 164316 (2010).
[28] C.-W. Huang, Y.-C. Lee, and Y.-P. Lee, J. Chem. Phys. **132**, 164303 (2010).
[29] J. C. Amicangelo, B. Golec, M. Bahou, and Y.-P. Lee, Phys. Chem. Chem. Phys. (submitted).
[30] J. C. Amicangelo and Y.-P. Lee, J. Phys. Chem. Lett. **1**, 2956 (2010).
[31] Y.-F. Lee and Y.-P. Lee, J. Chem. Phys. **134**, 124314 (2011).
[32] P. L. Raston and D. T. Anderson, J. Chem. Phys. **126**, 021106 (2007).
[33] Y.-P. Lee, Y.-J. Wu, and J. T. Hougen, J. Chem. Phys. **129**, 104502 (2008).
[34] P. L. Raston and D. T. Anderson, Phys. Chem. Chem. Phys. **8**, 3124 (2006).
[35] S. C. Kettwich, P. L. Raston, and D. T. Anderson, J. Phys. Chem. A **113**, 7621 (2009).
[36] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
[37] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[38] A. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[39] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[40] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[41] B. S. Ault, J. Phys. Chem. **91**, 4723 (1987).
[42] S. L. Laursen and G. C. Pimentel, J. Phys. Chem. **93**, 2328 (1989).
[43] S. L. Laursen and G. C. Pimentel, J. Phys. Chem. **94**, 8175 (1990).
[44] S. M. Resende and W. R. de Almeida, Mol. Phys. **91**, 635 (1997).
[45] P. Brana, B. Menendez, T. Fernandez, and J. A. Sordo, J. Phys. Chem. A **104**, 10842 (2000).
[46] See supplementary material at http://dx.doi.org/10.1063/1.3653988 for harmonic vibrational wavenumbers and IR intensities of three conformers of $\cdot CHClCHD_2$ and two conformers of $\cdot$CHDCHDCl calculated with the B3LYP/aug-cc-pVDZ method (Table S1), comparison of experimental line positions and relative intensities of chloroethene (C_2H_3Cl and $^{13}C_2H_3Cl$) in solid p-H_2 with predicted harmonic vibrational wavenumbers and relative intensities (Table S2), comparison of predicted line positions and intensities of *trans*-CHDCDCl, *cis*-CHDCDCl, and $CHClCD_2$ with experimental values (Table S3), and comparison of experimental line positions and relative intensities of known products with predicted harmonic vibrational wavenumbers and relative intensities (Table S4).
[47] Y.-C. Lee, V. Venkatesan, Y.-P. Lee, P. Macko, K. Didiriche, and M. Herman, Chem. Phys. Lett. **435**, 247 (2007).
[48] K. Sundararajan, K. Sankaran, K. S. Viswanathan, A. D. Kulkarni, and S. R. Gadre, J. Phys. Chem. A **106**, 1504 (2002).
[49] H. Tanskanen, L. Khriachtchev, J. Lundell, and M. Räsänen, J. Chem. Phys. **121**, 8291 (2004).
[50] Y.-J. Wu, X. Yang, and Y.-P. Lee, J. Chem. Phys. **120**, 1168 (2004).
[51] S. T. Collins, P. A. Casey, and G. C. Pimentel, J. Chem. Phys. **88**, 7307 (1988).
[52] D. C. McKean, G. P. McQuillan, A. H. J. Robertson, W. F. Murphy, V. S. Mastryukov, and J. E. Boggs, J. Phys. Chem. **99**, 8994 (1995).
[53] A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, Trans. Faraday Soc. **65**, 3172 (1969).
[54] M. P. Casassa, C. M. Western, F. G. Celli, D. E. Brinza, and K. C. Janda, J. Chem. Phys. **79**, 3227 (1983).
[55] L. R. Posey, Jr. and E. F. Barker, J. Chem. Phys. **17**, 182 (1949).
[56] Y.-J. Wu and B.-M. Cheng, Chem. Phys. Lett. **461**, 53 (2008).
[57] D. Forney, M. E. Jacox, and W. E. Thompson, J. Mol. Spectrosc. **170**, 178 (1995).
[58] L. Andrews, G. P. Kushto, M. Zhou, S. P. Willson, and P. F. Souter, J. Chem. Phys. **110**, 4457 (1999).
[59] J. Riehl and K. Morokuma, J. Chem. Phys. **100**, 8976 (1994).
[60] A. M. Mebel, K. Morokuma, and M. C. Lin, J. Chem. Phys. **103**, 3440 (1995).
[61] R. B. Barat and J. W. Bozzelli, J. Phys. Chem. **96**, 2494 (1992).