

Matrix Infrared Spectra and DFT Computations of 2*H*-Azirine Produced from Acetonitrile by Laser-Ablation Plume Radiation

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2*H*-azirine, a less known acetonitrile isomer, is observed in matrix IR spectra from the precursor exposed to radiation from laser ablation of transition-metals. Its vibrational characteristics confirm the previous results, and those for the deuterated and ^{13}C substituted isotopomers are also newly reported. The weak absorptions are traced to the low production yield due to its high energy and low extinction constants. IRC computations reveal smooth inter-conversion between 2*H*-azirine and CH_2NCH , providing a rationale for the observed variation of their relative contents during photolysis.

Key Words : 2*H*-azirine, Infrared, DFT, Matrix, Laser-ablation

Introduction

Acetonitrile, which is a common organic solvent and well known for its ability to form adducts with Lewis acids,¹ also generates various isomers and fragments.²⁻⁶ Many of them have been the subjects of recent spectroscopic and reaction dynamics studies. Especially inter-conversions between the cyano and isocyano isomers, formation of the cyclic derivatives, electron-trapping, and C-H bond dissociation have drawn much attention.^{2,3,6,7} These less stable species are mostly generated by photolysis of acetonitrile or larger nitrogen containing organic compounds and observed as trapped in cold matrix as well as in gas phase.¹⁻⁷

Recently it has been demonstrated that these photo-isomers and fragments can also be produced during co-deposition of the precursor with laser-ablation transition-metals.⁷⁻⁹ The radiation from metal plume by laser-ablation is an effective UV source, providing valuable opportunities to prepare the photo-chemical products.⁷⁻⁹ The matrix IR spectra of acetonitrile exposed to the radiation show strong absorptions of CH_2CNH and CH_3NC ,¹⁰ which are relatively stable isomers (Figure 1). The production yield of a photo-isomer largely depends on the energy relative to the precursor and other plausible photo-isomers.^{2,6-8} We have reported observation of CH_2NCH absorptions in the matrix IR spectra and suggested the possibility that it is produced *via* 2*H*-azirine (*cyc*- CH_2NCH).¹¹

Maier *et al.* have prepared 2*H*-azirine by photo-dissociation of vinyl azide (CH_2CHN_3) without information about its isotopomers.² In this paper, we report observation of 2*H*-azirine in the matrix IR spectra of CH_3CN exposed to the radiation of laser-ablated transition-metals, and possible inter-conversion to energetically comparable CH_2NCH . The *cyc*- CH_2NCH absorptions are turned out to be much weaker than those from CH_2NCH ,¹¹ making them difficult to designate. The vibrational characteristics of the deuterated and ^{13}C substituted isotopomers are also newly observed and correlate well with the DFT results.

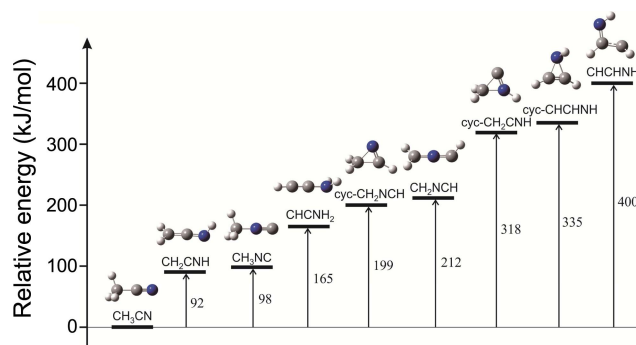


Figure 1. Energies of isomers relative to acetonitrile (computed with B3LYP/6-311++G(3df,3pd)).

Experimental

The 2*H*-azirine spectra shown in this report were recorded from samples prepared by co-deposition of acetonitrile with laser-ablated Hf atoms in excess argon at 10 K using a closed-cycle refrigerator (Air Products, Displex).¹⁰ However, other metals (groups 3-11 and actinides) also yield the same product absorptions although the intensities vary owing to different laser ablation plume radiation from specific metal surfaces. Therefore, these metal independent absorptions do not arise from metal containing species.

In our experiments, metal atoms and intense radiation from the laser ablation plume impinge on the depositing matrix sample. These methods have been described in detail in previous publications.¹² Reagent gas mixtures are typically 0.25-0.50% in argon. The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate, 10 ns pulse width) was focused onto the rotating metal target (Johnson-Matthey) using 5-10 mJ/pulse. After co-deposition, infrared spectra were recorded at 0.5 cm^{-1} resolution using a Nicolet 550 spectrometer with a Hg-Cd-Te range B detector. Then samples were irradiated for 20 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of

optical filters or annealed to allow further reagent diffusion.

Complementary density functional theory (DFT) calculations were carried out using the Gaussian 09 package,¹³ the B3LYP density functional,¹⁴ and 6-311++G(3df,3pd) basis sets for H, C, and N to provide a consistent set of vibrational frequencies and energies for the reaction product and its plausible isomers.^{2,3,11} Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis. Additional BPW91¹⁵ calculations were done to confirm the B3LYP results. The vibrational frequencies were calculated analytically, and the zero-point energy is included in the relative energy. Intrinsic reaction coordinate (IRC) calculations¹⁶ have been performed to link the transition state with the reactant and product.

Results and Discussion

2H-Azirine Absorptions. Figures 1-3 show the 2H-azirine (cyc-CH₂NCH) absorption regions. The product absorptions are marked “az” (for 2H-azirine), and their frequencies are listed along with the previously reported values and compared with the DFT results in Table 1. The 2H-azirine absorptions are mostly weak as shown in Figures 2-3, reflecting a low production yield. The product absorptions observed in the original deposition spectra remain unchanged on visible ($\lambda > 420$ nm) irradiation, slightly increase (5-10%) on uv ($240 < \lambda < 380$ nm) irradiation, and gradually decrease in annealing.

Spectral assignments have been done with help from the previously reported frequencies² and DFT values. The strongest CH₂ wagging absorption is observed at 971.2 cm⁻¹ along with its site absorptions at 975.4, 972.6, and 967.2

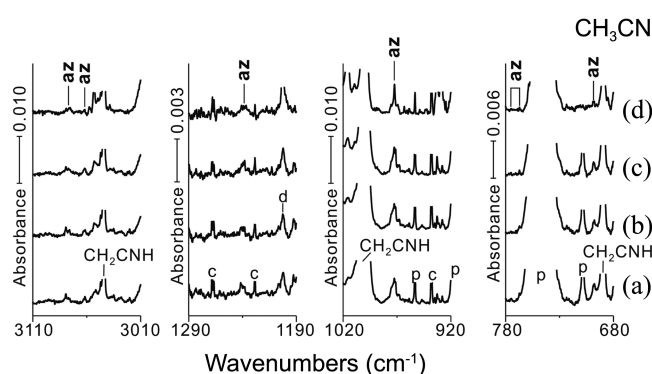


Figure 2. IR spectra in the 2H-azirine (cyc-CH₂NCH) absorption regions for CH₃CN co-deposited with laser-ablated Hf atoms in excess argon at 10 K and their variation. (a) 0.25% CH₃CN in Ar deposited for 1 h. (b) As (a) after photolysis ($\lambda > 420$ nm). (c) As (b) after photolysis ($240 < \lambda < 380$ nm). (d) As (c) after annealing to 28 K. az stands for 2H-azirine absorption, p indicates precursor absorption, and c denotes common absorption in CH₃CN experiments. CH₂CNH absorptions are also designated.

cm⁻¹, close to the previously reported values (978.7, 977.3, 974.4, and 971.5 cm⁻¹)² as shown in Table 1. Its D counterpart is newly observed at 781.9 cm⁻¹ (with site absorptions at 784.0 and 780.2 cm⁻¹), and the ¹³C counterpart at 961.9 cm⁻¹ (with site absorptions at 964.4 and 958.4 cm⁻¹). The C-H stretching absorption at 3078.5 carries its ¹³C counterpart at 3066.5 cm⁻¹ while the D counterpart is not observed in the congested region. The CH₂ anti-symmetric stretching band at 3061.3 cm⁻¹ is accompanied with its ¹³C counterpart at 3047.2 cm⁻¹. The C=N stretching absorption at 1668.3 cm⁻¹ shifts to 1654.3 and 1635.2 cm⁻¹ on deuteration and ¹³C substitution.

Table 1. Calculated Fundamental Frequencies of 2H-Azirine (cyc-CH₂NCH) Isotopomers in the Ground ¹A' State^a

Approximate Description	cyc-CH ₂ NCH					cyc-CD ₂ NCD					cyc- ¹³ CH ₂ N ¹³ CH				
	Obs ^b	B3LYP ^c	Int ^c	BPW91 ^d	Int ^d	Obs ^b	B3LYP ^c	Int ^c	BPW91 ^d	Int ^d	Obs ^b	B3LYP ^c	Int ^c	BPW91 ^d	Int ^d
A' C-H str.	3078.5, 3078.4 ^e	3207.6	1	3142.2	2	covered	2410.9	0	2359.3	1	3066.5	3195.3	1	3130.2	2
A'' CH ₂ as. str.	3061.3, 3061.5 ^e	3182.5	19	3120.1	20	covered	2374.4	12	2327.5	13	3047.2	3169.0	18	3106.9	19
A' CH ₂ s. str.	covered, 3005.6 ^e	3093.6	25	3031.3	26	2174.7	2236.8	14	2191.9	15	covered	3088.9	25	3026.6	26
A' C=N str.	1668.3, 1669.1 ^e , 1667.2 ^e	1754.7	11	1691.5	8	1654.3	1694.2	13	1634.4	9	1635.2	1720.9	11	1658.8	7
A' CH ₂ bend		1512.7	0	1464.7	0		1226.0	3	1203.0	2		1508.2	0	1460.3	0
A' C-C str.	1239.3, 1237.9, 1240.5 ^e , 1237.6 ^e	1267.2	10	1242.0	8		1077.9	2	1046.7	1	1203.9 , 1200.9	1231.0	12	1205.1	9
A'' CH ₂ rock		1119.1	2	1085.1	2		876.3	2	849.2	2		1109.4	2	1075.8	2
A' C-H ip bend		1048.3	1	1007.5	0		830.6	4	800.3	5		1040.8	1	1000.5	0
A' CH ₂ wag	975.4, 972.6, 971.2 , 967.2, 978.7 ^e , 977.3 ^e , 974.4 ^e , 971.5 ^e	1000.0	49	966.9	49	784.0, 781.9 , 780.2	811.3	15	779.9	13	964.4, 961.9 , 958.4	988.3	48	956.7	48
A'' CH ₂ twist		988.9	1	960.4	0		755.3	0	731.3	0		985.9	1	957.5	1
A'' C-H oop bend	771.8, 767.2, 772.9 ^e , 767.1 ^e	802.3	17	771.0	17	578.5 , 571.6	601.0	7	579.6	7	767.3 , 762.9	796.9	17	765.7	17
A' C-N str.	698.5	712.5	16	693.1	15	631.4	645.3	23	627.1	22	covered	700.2	15	591.0	14

^aFrequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cComputed with B3LYP/6-311++G(3df,3pd). ^dComputed with BPW91/6-311++G(3df,3pd). 2H-azirine has a C_s structure. ^eReported by Maier *et al.* (Ref. 2).

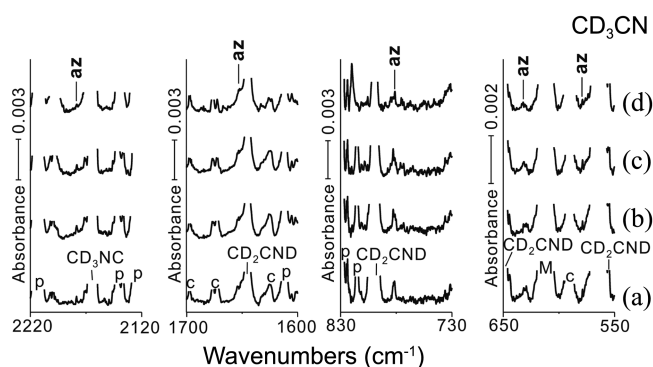


Figure 3. IR spectra in the cyc-CD₂NCD absorption regions for CD₃CN co-deposited with laser-ablated Hf atoms in excess argon at 10 K and their variation. (a) 0.50% CD₃CN in Ar deposited for 1 h. (b) As (a) after photolysis ($\lambda > 420$ nm). (c) As (b) after photolysis ($240 < \lambda < 380$ nm). (d) As (c) after annealing to 28 K. **az** stands for cyc-CD₂NCD absorption, p and M indicate precursor and metal containing product absorptions from Hf + CD₃CN reaction. c denotes common absorption in CD₃CN experiments. CD₂CND and CD₃NC absorptions are also designated.

Similarly the C-C stretching absorptions at 1239.3 cm⁻¹ leads to observation of its D and ¹³C counterparts at 781.9 and 964.4 cm⁻¹, and the C-H out-of-plane bending absorption at 771.8 cm⁻¹ its D and ¹³C counterparts at 578.5 and 767.3 cm⁻¹. The CH₂ symmetric stretching absorption previously reported at 3005.6 cm⁻¹,² however, is not discernible in our spectra, being covered by precursor absorption. Newly observed product absorption at 698.5 cm⁻¹ is assigned to the C-N stretching mode with its D counterpart at 631.4 cm⁻¹. The observed frequencies correlate reasonably with the DFT values as shown in Table 1 (0.950-0.980 of the B3LYP frequencies).

These observed product absorptions clearly show that 2*H*-azirine, a photo-isomer of acetonitrile, is produced along with other isomers and fragments by laser-ablation radiation. They are, however, much weaker than those of previously investigated CH₂CNH, CH₃NC, and CH₂NCH.^{2,3,11} Computations at B3LYP/6-311++G(3df,3pd) level show that CH₂CNH, CH₃NC, 2*H*-azirine, and CH₂NCH are 92, 98, 199, and 212 kJ/mol higher in energy than acetonitrile, respectively (Figure 1). The low production yield of this cyclic isomer evidently originates from its high energy.

However, it is still notable that the 2*H*-azirine absorptions are weaker than those from energetically comparable CH₂NCH.¹¹ DFT results reveal that its absorption constants are considerably smaller than those for CH₂NCH as shown in Table 1 (and Table 2 in Ref. 11). For example, the strongest CH₂ wagging band of 2*H*-azirine is eight times weaker than the strongest HCN bending band of CH₂NCH. Vibrational analysis indicates that the cyclic structure substantially decreases the amounts of dipole moment change for many of its vibrational modes. For instance, the C=N stretching mode is essentially a CNC anti-symmetric stretching mode for CH₂NCH, leading to the second strong band. However, it is mixed with the C-H stretching and CH₂ scissoring modes for 2*H*-azirine, the counteracting dipole moment changes

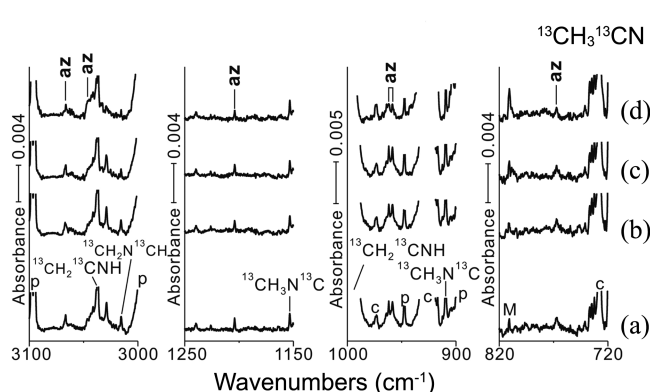


Figure 4. IR spectra in the cyc-¹³CH₂N¹³CH absorption regions for ¹³CH₃¹³CN co-deposited with laser-ablated Hf atoms in excess argon at 10 K and their variation. (a) 0.50% ¹³CH₃¹³CN in Ar deposited for 1 h. (b) As (a) after photolysis ($\lambda > 420$ nm). (c) As (b) after photolysis ($240 < \lambda < 380$ nm). (d) As (c) after annealing to 28 K. **az** stands for cyc-¹³CH₂N¹³CH absorption, and p and M indicate precursor and metal containing product absorptions from Hf + ¹³CH₃¹³CN reaction. c denotes common absorption in ¹³CH₃¹³CN experiments. ¹³CH₂¹³CNH and ¹³CH₃N¹³C absorptions are also designated.

resulting in a weak band.

Molecular Structure and Reactions. Figure 5 shows the B3LYP structures of CH₂NCH and 2*H*-azirine and transition state between them. NBO¹⁷ analysis suggests that the two C-N and N-C bonds in CH₂NCH are true double bonds (natural bond orders of 1.75 and 1.95), whereas those of 2*H*-azirine (cyc-CH₂NCH) are single and double bonds (natural bond orders of 0.95 and 1.96). The lower bond orders and structural strain in the cyclic configuration lead to the longer bonds in 2*H*-azirine. The transition state is 183 and 195 kJ/mol higher than CH₂NCH and 2*H*-azirine, and the single imaginary frequency (591 cm⁻¹) arises from the CNC bending mode, consistent with the fact that the conversion of 2*H*-azirine to CH₂NCH is ring-opening by breaking of the C-C bond.

The energetically comparable CH₂NCH and 2*H*-azirine were previously suggested to be inter-convertible. Intrinsic reaction coordinate (IRC)¹⁶ computations are carried out for

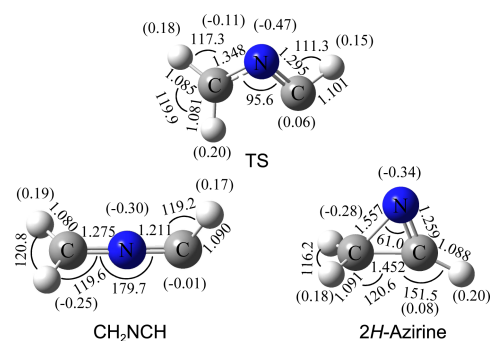


Figure 5. The B3LYP structures of CH₂NCH and 2*H*-azirine and transition state between them. The bond lengths and angles are in Å and degrees. The numbers in parentheses are the natural atomic charges.¹⁷

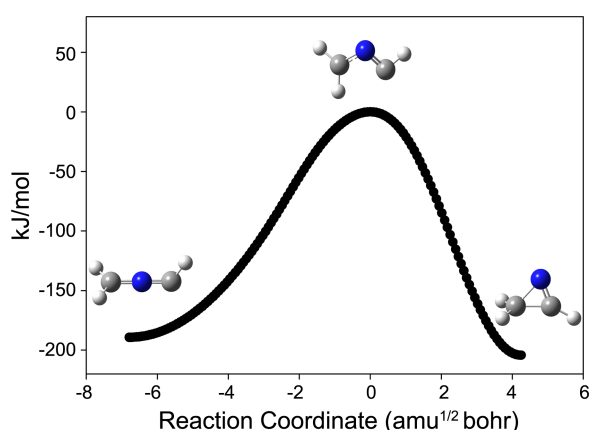


Figure 6. Intrinsic reaction coordinate (IRC)¹⁶ calculation between CH₂NCH and 2*H*-azirine.

the isomerization reaction between CH₂NCH and 2*H*-azirine (Figure 6), showing smooth conversion between the two photo-isomers of acetonitrile. These results support the previous assumption that cyclization with H migration from the methyl carbon to the nitrile carbon yields the 2*H*-azirine from acetonitrile, and following C-C bond dissociation leads to formation of CH₂NCH.¹¹ While the CH₂NCH absorptions nearly disappear on uv (240 λ <math>< 380</math> nm) irradiation after original deposition, the 2*H*-azirine absorptions increase slightly. This suggests that CH₂NCH not only photo-converts to 2*H*-azirine, but also proceed to other reactions, such as photo-fragmentation to CH₂NC in the matrix.^{5,7}

Conclusion

2*H*-Azirine (cyc-CH₂NCH) is produced during deposition of acetonitrile by laser-ablation radiation, and its absorptions are observed in the matrix IR spectra, mostly close to the previously reported frequencies. The absorptions of its deuterated and ¹³C substituted isotopomers are also newly reported in this work. The observed frequencies and isotopic shifts correlate well with the predicted values. The relatively low absorption intensities are traced to the low production yield due to its high energy and the small absorption constants. IRC computations reveal smooth inter-conversion between 2*H*-azirine and CH₂NCH, the energetically comparable isomers of CH₃CN. This corroborates the previous suggestion that 2*H*-azirine is produced *via* cyclization and H-migration of acetonitrile, and subsequent dissociation of the C-C bond of the cyclic compound leads to generation of CH₂NCH.

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