FORMATION AND IDENTIFICATION OF INTERSTELLAR MOLECULE LINEAR C5H FROM PHOTOLYSIS OF METHANE DISPERSED IN SOLID NEON

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ABSTRACT

Photolysis of methane dispersed (1/1000) in solid Ne at 3 K with vacuum-ultraviolet light from a synchrotron produced infrared absorption lines of several products, including new lines at 3319.3 and 1955.5 cm^{-1}. Based on experiments with isotopic labeling and results of quantum-chemical calculations, these lines are assigned to the C–H stretching and C=C stretching modes, respectively, of interstellar molecule linear C5H radicals.

Key words: astronomical data bases: miscellaneous – ISM: molecules – molecular data – stars: carbon

Acetylenic linear carbon-chain radicals C_nH play important roles in interstellar chemistry (Henning & Salama 1998; Kroto et al. 1987) and combustion (Fang et al. 2001). Up to $n = 8$, these radicals have been detected in interstellar molecular clouds and envelopes of evolving stars with large radio telescopes (Bell et al. 1999). In the laboratory, these singly hydrogenated, long-chain, carbon radicals have been identified mostly by microwave spectra ($n \leqslant 14$; Gottlieb et al. 1998). Other spectral data of carbon chains up to $C_{10}H$ were obtained from fluorescence (Hoshina et al. 1998), cavity ring-down absorption (Linnartz et al. 1998), and photoionization (Ding et al. 2002). Infrared (IR) absorption spectra that provide information about the bonding and structures of molecules are limited relative to other optical spectra for C_nH radicals, of which IR spectra of C_2H (Shepherd & Graham 1987; Jacox & Olson 1987; Wu & Cheng 2008), C_3H (Jacox & Milligan 1974; Huang & Graham 1990), C_4H (Shen et al. 1990), and C_6H (Doyle et al. 1991) were first identified in matrix-isolation experiments. Vibrational characterization of longer carbon chains has not yet been achieved, and the IR spectrum of C_5H has been lacking. Here we report the generation of C_5H radicals by vacuum-ultraviolet (VUV) photolysis of methane isolated in solid Ne at 3 K and the identification of its IR fundamental vibrational modes. This information will be useful for laboratory investigation and astronomical observation of this species.

For C_5H radicals, various isomers have been predicted and reported in various possible conformations. Rotational spectra of linear C_5H (*l*-C_5H; Gottlieb et al. 1986) and cyclic C_5H (*c*-C_5H; Apponi et al. 2001) were recorded in the microwave region. In space, *l*-C_5H has been detected in the envelope of carbon star IRC+10216 (Cernicharo et al. 1986) and in cold dark cloud TMC-1 (Cernicharo et al. 1987). Crawford et al. (1999) applied high-level computational methods based on a coupled-cluster approximation to investigate the structure and energetics of isomers of C_5H radicals; seven possible structures of C_5H were identified, and their vibrational wavenumbers and IR intensities were calculated. An experimental investigation of the IR absorption of C_5H is thus timely.

To generate C_5H, we irradiated a Ne matrix containing methane (1/500 or 1/1000) at an end-station that comprises

a refrigerator operated at 3 K coupled to a VUV undulator of a synchrotron (Wu & Cheng 2008; Wu et al. 2008). IR absorption spectra were recorded at various stages of experiments with an interferometric spectrometer (Bomem, DA8) equipped with a KBr beamsplitter and an MCT detector (cooled to 77 K) to cover the spectral range 500–5000 cm^{-1}. Spectra with 400 scans and resolution 0.5 cm^{-1} were typically recorded at each stage.

In the vacuum-ultraviolet region, the absorption of gaseous methane begins at 145 nm with a cross section about 0.003 Mb (1 Mb = 10^{-22} m^2), and increases monotonically and continuously to smaller wavelengths; these cross sections are greater than 10 Mb for $\lambda < 134$ nm (Lee et al. 2001). To photolyze methane efficiently, we selected radiation at 130 nm at which the gaseous cross section is 18 Mb. Irradiation at 130 nm of CH_4 in a Ne matrix for 2 hr caused the intensities of lines of CH_4 to decrease by about 40% and produced various products—carbon clusters and hydrocarbons including CH (Botterud et al. 1973), C_2H_2 (Wu & Cheng 2008), C_2H_3 (Wu et al. 2008), C_2H_4, C_3 (Matsumura et al. 1988), C_3H (Jacox & Milligan 1974; Huang & Graham 1990), C_4 (Wu & Cheng 2008), C_4H (Shen et al. 1990), C_4H_2 (Wu & Cheng 2008), C_5 (Forney et al. 1996), C_6 (Wu & Cheng 2008), and C_7 (Forney et al. 1996); the IR absorption lines of these photoproducts are listed in Table 1.

Figure 1(a) shows a partial difference IR absorption spectrum of a sample CH_4/Ne (1/1000) after photolysis at 130 nm for 2 hr; this difference spectrum was derived on subtracting the spectrum recorded after irradiation from the preceding spectrum following deposition. Photoproducts of known species in these spectral regions are marked in the figure. Two absorption lines appearing at 3319.3 and 1955.5 cm^{-1} (denoted*) are previously unreported. To identify the carriers of unassigned lines based on isotopic shifts and line splitting, we undertook experiments with isotopic substitution of methane (CD_4, CH_2D_2, CH_4/CD_4, $^{12}CH_4/^{13}CH_4$, and $^{13}CH_4$) dispersed in solid Ne under the same conditions of VUV photolysis; the difference IR absorption spectra for these isotopic samples are shown also in Figure 1, and the photoproducts and their IR absorption lines from isotopic samples are listed in Appendices A and B. Photolysis of a CD_4/Ne sample at 130 nm produced pertinent lines shifted to 2535.1 cm^{-1} and 1917.9 cm^{-1}, as shown in Figure 1(b); the shifts yield isotopic ratios 0.7637 and 0.9808, respectively. For a $^{13}CH_4$/Ne sample, the corresponding lines appeared at 3295.6

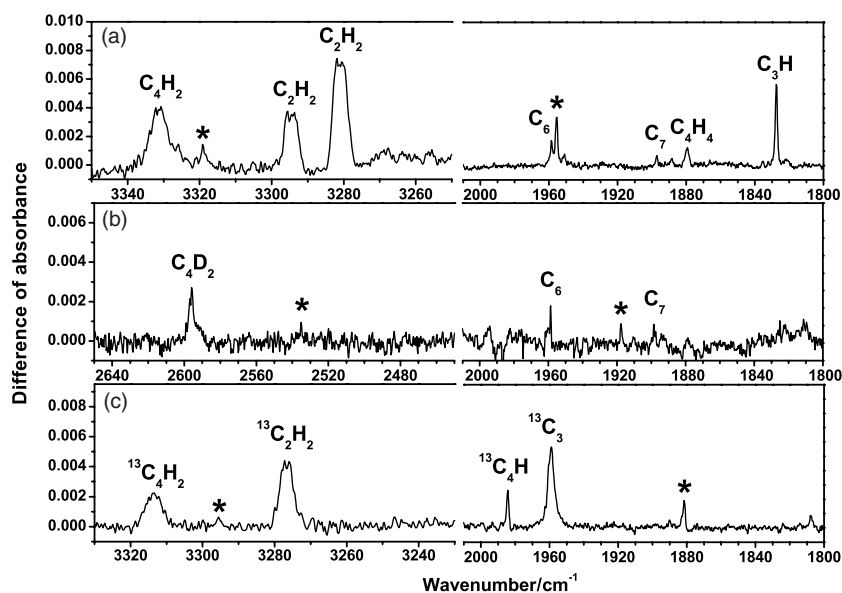[4] Author to whom any correspondence should be addressed.

Figure 1. Partial IR spectra of samples of methane/Ne (1/1000) at 3 K with isotopic variants after irradiation at 130 nm for 2 hr: (a) CH_4/Ne, (b) CD_4/Ne, and (c) $^{13}CH_4$/Ne.

Table 1
Vibrational Wavenumbers of Observed Photoproducts

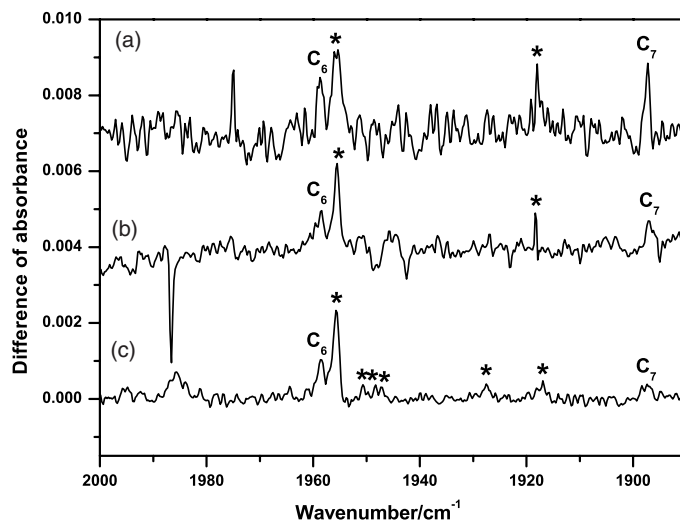| Photoproduct	Line Positions (cm^{-1})
CH	2733.0
C_2H_2	3281.1 (ν_3), 731.7 (ν_5), 1329.4 ($\nu_4+\nu_5$), 3295.6 ($\nu_3+\nu_4+\nu_5$)
C_2H_3	1357.2 (ν_5), 895.2 (ν_8)
C_2H_4	949.9 (ν_7), 2982.8 (ν_{11}), 1441.6 (ν_{12}),
C_3	2043.5 (ν_3)
C_3H	1827.5 (ν_2)
C_4	1547.2 (ν_3)
C_4H	2063.2 (ν_2)
C_4H_2	3331.0 (ν_4), 629.6 (ν_8)
C_4H_4	1879.6 (?)
C_5	2165.5 (ν_3)
C_5H	3319.3 (ν_1), 1955.5 (ν_3)
C_6	1958.6 (ν_4)
C_7	1897.3 (ν_5), 2135.0 (ν_4)

Figure 2. Partial difference IR absorption spectra of methane in Ne matrix samples at 3 K with isotopic variants after irradiation at 130 nm for 2 hr: (a) CH_2D_2/Ne (1/1000), (b) CH_4/CD_4/Ne (0.5/0.5/1000), and (c) $^{12}CH_4$/$^{13}CH_4$/Ne (0.9/0.1/500).

and 1881.5 cm^{-1}, as shown in Figure 1(c), consistent with ^{13}C-isotopic ratios 0.9929 and 0.9622, respectively. For a sample of CH_2D_2/Ne or CH_4/CD_4/Ne under the same conditions, as shown in Figures 2(a) and (b), the appearance of only two pertinent lines at 1955.5 and 1917.9 cm^{-1} indicates that the carrier contains only one hydrogen. Considering the formation of these photoproducts and the absence of absorption features of l-C_6H, the new lines at 3319.3 and 1955.6 cm^{-1} might correspond to l-C_5H. Comparison of known D-isotopic ratios of C–H stretching modes of C_nH (0.7705 for C_2H (Wu & Cheng 2008), 0.7486 for C_3H (Jacox & Milligan 1974), and 0.7799 for C_4H (Shen et al. 1990)), and of C=C stretching modes of C_nH (0.9478 for C_2H (Wu & Cheng 2008), 0.9706 for C_3H (Jacox & Milligan 1974), 0.9870 for C_4H (Shen et al. 1990), and 0.9534 for C_6H (Doyle et al. 1991)) indicates that our observed D-isotopic ratio is reasonable for a monohydride carbon species.

To determine definitely the carbon number of this monohydride carbon species, we performed an experiment with the mixed isotopic sample of $^{12}CH_4$/$^{13}CH_4$/Ne (0.9/0.1/500) under the same conditions of VUV photolysis; the difference in IR absorption spectrum for these isotopic samples is displayed also in Figure 2(c). The single line at 1955.5 cm^{-1} observed in the $^{12}CH_4$/Ne experiment was split into six

components in the $^{12}CH_4$/$^{13}CH_4$/Ne experiment—one intense line at 1955.5 cm^{-1} and five weak satellites at 1950.7, 1948.3, 1947.3, 1927.5, and 1917.0 cm^{-1}. The intense feature at 1955.5 cm^{-1} is associated with l-$^{12}C_5H$. Considering the composition ratio of ^{12}C/^{13}C in this experiment, we expect the formed carbon monohydride to contain only one ^{13}C atom in the mixed isotopic carbon chain. Additionally, supposing five carbon atoms in this molecule, there are five expected separate isotopic variants—l-$^{13}C^{12}C^{12}C^{12}C^{12}CH$, l-$^{12}C^{13}C^{12}C^{12}C^{12}CH$, l-$^{12}C^{12}C^{13}C^{12}C^{12}CH$, l-$^{12}C^{12}C^{12}C^{13}C^{12}CH$, and l-$^{12}C^{12}C^{12}C^{12}C^{13}CH$—for this monohydride carbon species. Our result showing five extra weak satellite features at 1950.7, 1948.3, 1947.3, 1927.5, and 1917.0 cm^{-1} in Figure 2(c) is hence consistent with this carrier containing five carbon atoms.

Our experimental findings have been corroborated by accurate calculations of fundamental vibrational wavenumbers of gaseous C_5H. According to the previous theoretical

Table 2
Vibrational Wavenumbers (cm^{-1}) of *l*-C$_5$H Predicted with Various Computational Methods or Observed Experimentally

Isotope	Mode	This Work			Experiment
		EOMEA-CCSD/TZ2P[a]	EOMEA-CCSD/cc-pVDZ		
		Harmonic	Harmonic	Anharmonic	
C$_5$H	$\nu_1(\sigma^+)$	3478.1	3487.9	3347.5	3319.3 (−28.2)[b]
	$\nu_2(\sigma^+)$	2090.6	2094.3	2050.7	
	$\nu_3(\sigma^+)$	1944.8	1960.9	1941.1	1955.5 (+14.4)
	$\nu_4(\sigma^+)$	1419.6	1423.1	1408.0	
	$\nu_5(\sigma^+)$	747.4	750.8	713.8	
C$_5$D	$\nu_1(\sigma^+)$	. . .	2674.8	2594.6	2535.1 (−59.5)
	$\nu_2(\sigma^+)$	. . .	1998.4	1966.8	
	$\nu_3(\sigma^+)$	. . .	1955.0	1931.1	1917.9 (−13.2)
	$\nu_4(\sigma^+)$	. . .	1411.1	1395.2	
	$\nu_5(\sigma^+)$	. . .	740.2	687.0	
^{13}C$_5$H	$\nu_1(\sigma^+)$	. . .	3471.1	3336.0	3295.6 (−40.4)
	$\nu_2(\sigma^+)$	. . .	2017.0	1976.0	
	$\nu_3(\sigma^+)$	. . .	1883.8	1865.4	1881.5 (+16.1)
	$\nu_4(\sigma^+)$	. . .	1367.8	1354.3	
	$\nu_5(\sigma^+)$	. . .	722.0	688.0	

Notes.
[a] Data from Crawford et al. (1999).
[b] The deviation between experimental and calculated wavenumbers is specified in parentheses.

(Haubrich et al. 2002; Crawford et al. 1999) and experimental (McCarthy & Thaddeus 2008) investigations, the most energetically stable isomer of this radical is *l*-C$_5$H. We have employed the electron-attachment equation-of-motion coupled-cluster technique (Nooijen & Bartlett 1996; EOMEA-EOMCC) and the correlation-consistent polarized-valence double-zeta (cc-pVDZ) basis set of Dunning (1989). Other computational details follow closely the original work of Crawford et al. (1999). The fundamental wavenumbers have been computed using second-order perturbation theory from an initial harmonic-oscillator rigid-rotor approximation (Stanton & Gauss 2000). An accurate theoretical determination of the fundamental σ^+ wavenumbers is crucial for a validation of our experimental assignment, because the commonly reported harmonic wavenumbers, bearing an error 100–200 cm^{-1}, give little information on the identity of the analyzed species in the spectrally congested region above 3000 cm^{-1}. The calculations have been performed with the CFOUR program.[5] We considered explicitly three isotopically substituted species, C$_5$H, C$_5$D, and ^{13}C$_5$H, which correspond directly to the species observed in our experiments. The results of these calculations are presented in Table 2. The mean absolute deviation between the corresponding computed and measured fundamental σ^+ wavenumbers of C$_5$H (and its isotopic variants) is 28 cm^{-1}. This agreement is deemed entirely satisfactory when one takes into account that the experiment is performed in a solid neon matrix, whereas the calculations pertain to an iso-

lated molecule as in the gaseous phase. In general, the solid neon matrix shift is expected to be within ±1% of the fundamental value (Jacox 1993), which correlates satisfactorily with the slightly larger discrepancies observed for the carbon–hydrogen stretching wavenumbers. These deviations might be decreased on employing a larger basis set in the calculations, but the resulting theoretical framework would be expensive. Another, and potentially much more important, source of the observed discrepancy can be the Renner–Teller effect expected for C$_5$H, a typical linear system with a degenerate electronic ground state. We observed a manifestation of this effect during our calculations of anharmonic wavenumbers for the π vibrational states: a simple approximation of the potential energy about the equilibrium position up to quartic terms yielded an entirely unphysical description of the anharmonic couplings between separate π vibrational modes. We thus expect that the present theoretical results constitute a strong confirmation of our experimental assignment of the observed spectral lines to *l*-C$_5$H in its isotopic variants.

In summary, we have demonstrated a method to produce long carbon-chain molecules in a neon matrix by photolysis of CH$_4$ with vacuum-ultraviolet light. Using this method, we generated and identified linear C$_5$H radicals. Based on observed D- and ^{13}C-isotopic shifts, line splittings and theoretical predictions of line positions, IR intensities and isotopic ratios of *l*-C$_5$H, the absorption features at 3319.3 and 1955.5 cm^{-1} are assigned to the C–H stretching and C=C stretching modes of *l*-C$_5$H.

APPENDIX A

Table A1 shows vibrational wavenumbers of observed photoproducts of a CD$_4$/Ne (1/1000) matrix sample at 3 K after irradiation at 130 nm for 2 hr.

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[5] CFOUR, Coupled Cluster techniques for Computational Chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowicz, M. E. Varner, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

Table A1
Vibrational Wavenumbers of Observed Photoproducts of a CD_4/Ne (1/1000)
Matrix Sample at 3 K After Irradiation at 130 nm for 2 hr

Photoproducts	Line Position (cm^{-1})
CD	2030.7 (?)
C_2D_2	2436.5 (ν_3), 539.1 (ν_5)
C_2D_3	704.0 (ν_8)
C_2D_4	720.5 (ν_7), 2339.2 (ν_9)
C_3	2043.5 (ν_3)
C_3D	1773.1 (ν_2)
C_4	1547.2 (ν_3)
C_4D	2052.7 (ν_2)
C_4D_2	2596.5 (ν_4)
C_5	2165.5 (ν_3)
C_5D	2535.1 (ν_1), 1917.9 (ν_3)
C_6	1958.6 (ν_4)
C_7	1897.3 (ν_5), 2135.0 (ν_4)

APPENDIX B

Table B1 shows vibrational wavenumers of observed photoproducts of $^{13}CH_4/Ne$ (1/1000) matrix sample at 3 K after irradiation at 130 nm for 2 hr.

Table B1
Vibrational Wavenumbers of Observed Photoproducts of $^{13}CH_4/Ne$ (1/1000)
Matrix Sample at 3 K After Irradiation at 130 nm for 2 hr

Photoproducts	Line Position (cm^{-1})
^{13}CH	2725.7
$^{13}C_2H_2$	3276.3 (ν_3), 729.9 (ν_5), 1318.1 ($\nu_4+\nu_5$)
$^{13}C_2H_3$	1351.3 (ν_5), 888.9 (ν_8)
$^{13}C_2H_4$	945.0 (ν_7), 2973.0 (ν_{11})
$^{13}C_3$	1958.7 (ν_3)
$^{13}C_3H$	1761.9 (ν_2)
$^{13}C_4$	1487.2 (ν_3)
$^{13}C_4H$	1984.3 (ν_2)
$^{13}C_4H_2$	3313.6 (ν_4)
$^{13}C_5$	2094.0 (ν_3)
$^{13}C_5H$	3295.6 (ν_1), 1881.5 (ν_3)
$^{13}C_6$	1890.2 (ν_4) ?
$^{13}C_7$	1823.6 (ν_5) ?

REFERENCES

Apponi, A. J., Sanz, M. E., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2001, ApJ, 547, L65
Bell, M. B., Feldman, P. A., Watson, J. K. G., McCarthy, M. C., Travers, M. J., Gottlieb, C. A., & Thaddeus, P. 1999, ApJ, 518, 740
Botterud, I., Lofthus, A., & Veseth, L. 1973, Phys. Scr., 8, 218
Cernicharo, J., Gúelin, M., & Walmsley, C. M. 1987, A&A, 172, L5
Cernicharo, J., Kahane, C., Gómez-González, J., & Gúelin, M. 1986, A&A, 167, L5
Crawford, T. D., Stanton, J. F., Saeh, J. C., & Schaefer, H. F. 1999, J. Am. Chem. Soc., 121, 1902
Ding, H., Pino, T., Güthe, F., & Maier, J. P. 2002, J. Chem. Phys., 117, 8362
Doyle, T. J., Shen, L. N., Rittby, C. M. L., & Graham, W. R. M. 1991, J. Chem. Phys., 95, 6224
Dunning, T. H., Jr. 1989, J. Chem. Phys., 90, 1007
Fang, D.-C., Harding, L. B., Klippenstein, S. J., & Miller, J. A. 2001, Faraday Discuss., 119, 207
Forney, D., Freivogel, P., Grutter, M., & Maier, J. P. 1996, J. Chem. Phys., 104, 4954
Gottlieb, C. A., Gottlieb, E. W., & Thaddeus, P. 1986, A&A, 164, L5
Gottlieb, C. A., McCarthy, M. C., Travers, M. J., Grabow, J.-U., & Thaddeus, P. 1998, J. Chem. Phys., 109, 5433
Haubrich, J., Mühlhäuser, M., & Peyerimhoff, S. D. 2002, J. Phys. Chem. A, 106, 8201
Henning, T., & Salama, F 1998, Science, 282, 2204
Hoshina, K., Kohguchi, H., Ohshima, Y., & Endo, Y. 1998, J. Chem. Phys., 108, 3465
Huang, J. W., & Graham, W. R. M. 1990, J. Chem. Phys., 93, 1583
Jacox, M. E. 1993, J. Phys. Chem. Ref. Data, 3, 7
Jacox, M. E., & Milligan, D. E. 1974, Chem. Phys., 4, 45
Jacox, M. E., & Olson, W. B. 1987, J. Chem. Phys., 86, 3134
Kroto, H. W., Heath, J. R., O'Brain, S. C., Curl, R. F., & Smalley, R. E. 1987, ApJ, 314, 352
Lee, A. Y. T., Yung, Y. L., Cheng, B. M., Bahou, M., Chung, C. Y., & Lee, Y. P. 2001, ApJ, 551, L93
Linnartz, H., Motylewski, T., & Maier, J. P. 1998, J. Chem. Phys., 109, 3819
Matsumura, K., Kanamori, H., Kawaguchi, K., & Hirota, E. 1988, J. Chem. Phys., 89, 3491
McCarthy, M. C., & Thaddeus, P. 2008, J. Chem. Phys., 122, 174308
Nooijen, M., & Bartlett, R. J. 1996, J. Chem. Phys., 102, 3629
Shen, L. N., Doyle, T. J., & Graham, W. R. M. 1990, J. Chem. Phys., 93, 1597
Shepherd, R. A., & Graham, W. R. M. 1987, J. Chem. Phys., 86, 2600
Stanton, J. F., & Gauss, J. 2000, Int. Rev. Phys. Chem., 19, 61
Wu, Y.-J., & Cheng, B.-M. 2008, Chem. Phys. Lett., 461, 53
Wu, Y.-J., Lin, M.-Y., Cheng, B.-M., Chen, H.-F., & Lee, Y.-P. 2008, J. Chem. Phys., 128, 204509