

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/221972021>

Synthesis and Microwave Spectrum of Vinyl Isoselenocyanate ($\text{H}_2\text{C}=\text{CHNCSe}$), a Compound with a Quasi linear CNCSe Chain

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2012

Impact Factor: 2.69 · DOI: 10.1021/jp301803z · Source: PubMed

CITATIONS

2

READS

39

4 AUTHORS, INCLUDING:



Svein Samdal

University of Oslo

174 PUBLICATIONS 2,618 CITATIONS

SEE PROFILE



Arne Joakim Bunkan

Max Planck Institute for Chemistry

11 PUBLICATIONS 37 CITATIONS

SEE PROFILE



Jean-claude Guillemin

Ecole Nationale Supérieure de Chimie de Ren...

385 PUBLICATIONS 3,379 CITATIONS

SEE PROFILE

Synthesis and Microwave Spectrum of Vinyl Isoselenocyanate ($\text{H}_2\text{C}=\text{CHNCSe}$), a Compound with a Quasilinear CNCSe Chain

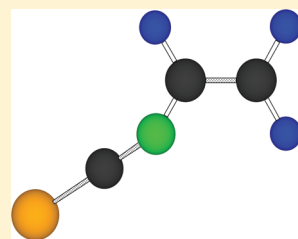
Harald Møllendal,^{*,†} Svein Samdal,[†] Arne Joakim C. Bunkan,[†] and Jean-Claude Guillemin^{*,‡}

[†]Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway

[‡]Sciences Chimiques de Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France

S Supporting Information

ABSTRACT: The first α,β -unsaturated isoselenocyanate, vinyl isoselenocyanate ($\text{H}_2\text{C}=\text{CHNCSe}$), has been synthesized, and its microwave spectrum has been investigated in the 11.5–77.0 GHz spectral range. The microwave work was augmented by quantum chemical calculations using four different methods, namely, CCSD(T), CCSD, B3LYP, and M062X, with the cc-pVTZ basis set. It is generally assumed that two rotamers having the isoselenocyanide group in an antiperiplanar or a synperiplanar position can exist for this compound. However, these four methods all predict that there is only *one* rotameric form of the molecule, namely, the antiperiplanar form. The CNC angle of the antiperiplanar rotamer is calculated to vary from 151° to 170° depending on the quantum chemical methodology. CCSD(T) and B3LYP potential functions of the in-plane CNC bending vibrations were calculated. These functions have one shallow minimum corresponding to the antiperiplanar form. The spectra of the ground and one vibrationally excited state of this rotamer were assigned. Spectral searches for the synperiplanar form were performed but were not successful, so this form must have a relatively high energy, if it exists at all. The vibrationally excited state is presumably the lowest in-plane bending vibration of the CNC angle. Relative intensity measurements yielded a very low frequency of $18(25) \text{ cm}^{-1}$ for this vibration. The large-amplitude vibration of this mode suggests that this compound should rather be regarded as having a quasilinear CNCSe link of atoms than a rigid, bent antiperiplanar form.



■ INTRODUCTION

Few reports of the spectroscopic and structural properties of gaseous isoselenocyanates have found their way into the chemical literature. The rotational¹ and vibrational² spectra of the simplest member of this family, isoselenocyanic acid (HNCSe), were investigated in 1984. This compound was assumed to have a slightly bent ($\sim 5^\circ$) NCSe chain of atoms and an HNC angle as large as 140° ,¹ instead of approximately 120° expected for an sp^2 -hybridized nitrogen atom. The lowest bending vibration² has a frequency of 419 cm^{-1} . The ratio between the A rotational constant and the lowest bending vibration is 0.13 ,¹ much larger than 0.01 , which would be typical for a “rigid” molecule.¹ Vibration and rotation are therefore not well-separated, and isoselenocyanic acid is therefore not a rigid, bent molecule but can best be classified as a “quasilinear” compound.^{1,3}

Theoretical treatments by Yamada et al.⁴ of quasilinear molecules, Bunker and Howe⁵ of triatomic molecules, and Koput⁶ and Koput et al.^{7,8} of quasisymmetric top molecules found that this phenomenon can occur for compounds having low-frequency anharmonic bending modes resulting in extreme centrifugal distortion behavior, unusual variation of vibration–rotation constants upon excitation of bending modes, and unusual Coriolis interactions.

In 1974, Franklin et al.⁹ investigated the infrared spectra of several alkyl isoselenocyanates in the gas, solid, and liquid

states. In the case of CH_3NCSe , they concluded that the methyl group of this compound has essentially free rotation. In the 1986 microwave (MW) spectroscopic investigation of Sakaizumi et al.¹⁰ of the same compound, only the A -species lines of the internal rotation of the methyl group were assigned in a very dense MW spectrum. A partial r_0 structure was determined. The NCSe link of atoms was assumed to be linear, and the CNC bond angle was now found to be $157(4)^\circ$, 17° larger than the HNC angle in HNCSe .¹

In a MW study¹¹ of the next homologue, $\text{CH}_3\text{CH}_2\text{NCSe}$, the spectrum of one conformer was assigned. This rotamer has a CCCN synclinal (obsolete: *cis*) conformation. The CNC angle was determined to be approximately 158° ,¹¹ about the same as in CH_3NCSe .¹⁰

In two more recent MW reinvestigations of CH_3NCSe by Koput et al.,^{7,8} it was found that this molecule can indeed be characterized as a quasisymmetric top. A potential function for the CNC bending vibration, which is the fundamental with the lowest frequency, was derived and found to be strongly anharmonic and to have a barrier to linearity of the CNCSe skeleton of only 290 J/mol (24 cm^{-1}).⁸ The energy of the ground vibrational state was found to be higher than the barrier

Received: February 23, 2012

Revised: March 22, 2012

Published: March 24, 2012

to linearity by only 2.4 cm^{-1} . Moreover, the first vibrationally excited state of the CNC bending vibration was calculated to have an energy that is 31.6 cm^{-1} higher than the energy of the ground vibrational state according to the potential function derived by these workers.⁸ The equilibrium CNC bond angle was found to be 161.3° , and the barrier to internal rotation of the methyl group was estimated to be as low as 22 J/mol (1.8 cm^{-1}).⁸ All of these results justify the categorization of CH_3NCSe as a quasisymmetric top.

The isoselenocyanide group is bonded to an sp^3 -hybridized carbon atom in both CH_3NCSe and $\text{CH}_3\text{CH}_2\text{NCSe}$. The bonding situation in the title compound, vinyl isoselenocyanate ($\text{H}_2\text{C}=\text{CHNCSe}$), is different from this in that the said group is now bonded to an sp^2 -hybridized carbon atom of the vinyl group. Electron conjugation of the π -electrons of the carbon–carbon double bond of the vinyl group with the π -electrons of the isoselenocyanide group is now possible. This effect is not present in CH_3NCSe and $\text{CH}_3\text{CH}_2\text{NCSe}$. It is elementary that electron conjugation can influence the structural, conformational, and dynamical properties significantly, and the role this effect can have was one reason for the present investigation of $\text{H}_2\text{C}=\text{CHNCSe}$.

Vinyl isoselenocyanate has not received much attention in the past, but one quantum chemical study by Badawi et al.¹² of the conformational and dynamical properties of this compound, as well as its oxygen ($\text{H}_2\text{C}=\text{CHNCO}$) and sulfur ($\text{H}_2\text{C}=\text{CHNCS}$) analogues, has appeared. Their MP2/6-311++G** calculations¹² predicted that there are two planar forms of all three vinyl isocyanates, namely, a CCNC antiperiplanar (CCNC dihedral angle = 180°) and a synperiplanar (CCNC dihedral angle = 0°) rotamer. Models of two such conformers with atom numbering are depicted in Figure 1 in the case of $\text{H}_2\text{C}=\text{CHNCSe}$. These forms of vinyl isoselenocyanate are hereafter referred to as **ap** and **sp**, respectively.

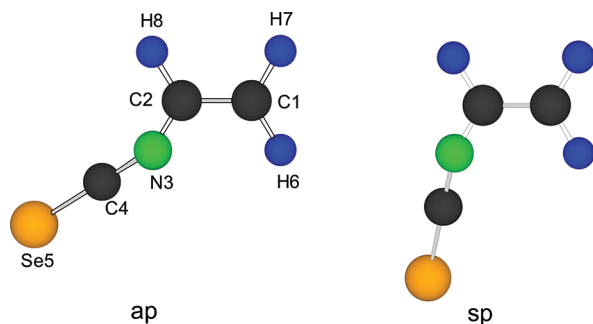


Figure 1. Models of the antiperiplanar (**ap**) and synperiplanar (**sp**) forms of $\text{H}_2\text{C}=\text{CHNCSe}$. Atom numbering is indicated on **ap**. The C1C2N3C4 dihedral angle is 180° in **ap** and 0° in **sp**.

The MP2 energy difference between **sp** and **ap** is 2.42 kJ/mol , with **ap** as the lowest-energy form, and the theoretical C2N3C4 angle is 152.0° in **sp** and 148.2° in **ap**.¹² The in-plane C2N3C4 bending vibration (ν_{13}) was calculated to be as low as 83 cm^{-1} in **ap** and 57 cm^{-1} in **sp**. A frequency claimed to be the torsion about the C2–N3 bond (ν_{18}) was calculated to have a frequency of 66 cm^{-1} in **ap** and 96 cm^{-1} in **sp**.¹²

Microwave studies have been reported for vinyl isocyanate ($\text{H}_2\text{C}=\text{CHNCO}$)¹³ and vinyl isothiocyanate ($\text{H}_2\text{C}=\text{CHNCS}$).¹⁴ Both a synperiplanar and an antiperiplanar conformer were found for vinyl isocyanate,¹³ whereas only the spectrum of the antiperiplanar rotamer was assigned for the

sulfur congener.¹⁴ The CNC angle, which dictates the degree of nonlinearity, was determined to be $142.4(5)^\circ$ in the antiperiplanar form and $138.4(15)^\circ$ in the synperiplanar conformer of $\text{H}_2\text{C}=\text{CHNCO}$,¹³ whereas a value of 137.6° was assumed for this angle in the antiperiplanar rotamer of $\text{H}_2\text{C}=\text{CHNCS}$.¹⁴ Complex and intense patterns of vibrationally excited states were observed for both these two compounds, but there is no indication from these excited states of prominent anharmonicity typical for quasilinearity.^{13,14}

It would be of interest to extend experimental studies of the physical properties to the corresponding seleno compound, but no reports of its synthesis were available. We therefore decided to perform the first preparation of $\text{H}_2\text{C}=\text{CHNCSe}$, which is reported herein. Quasilinearity of the CNCSe chain of atoms, which manifests itself in a complex pattern of vibrationally excited states, might exist in vinyl isoselenocyanate in addition to the problem associated with a possible conformational equilibrium involving **ap** and **sp**. An experimental method characterized by high resolution is required to cope with both the conformational and dynamical problems foreseen for this compound. MW spectroscopy, with its extreme accuracy and resolution, meets this requirement and is therefore the method of choice. The experimental work was augmented with high-level quantum chemical calculations, which were undertaken to obtain information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

EXPERIMENTAL SECTION

Synthesis. Into a one-necked cell equipped with a stopcock were introduced under nitrogen vinyl isocyanide (530 mg, 10 mmol),¹⁵ chloroform (10 mL), selenium powder (950 mg, 12 mmol), and few drops of tri-*n*-trioctylamine. The mixture was immersed in a liquid nitrogen bath and degassed. The stopcock was closed, and the mixture was heated at 60°C overnight. The cell was then adapted to a vacuum line equipped with a U-tube with stopcocks and immersed in a bath cooled at -45°C . The solution was heated to 60°C and distilled in vacuo (0.1 mbar). The vinyl isoselenocyanate was selectively trapped at -45°C . A second distillation can be performed to obtain a very pure sample. Yield: 37%, 488 mg. bp_{0.1 mbar} 40°C . ^1H NMR (CDCl_3 , 400 MHz) δ 5.18 (d, 1H, $^3J_{\text{HHcis}} = 7.9\text{ Hz}$, $\underline{\text{HCH}}$), 5.42 (d, 1H, $^3J_{\text{HHtrans}} = 15.2\text{ Hz}$, $\underline{\text{HCH}}$), 6.16 (dd, 1H, $^3J_{\text{HHcis}} = 7.9\text{ Hz}$, $^3J_{\text{HHtrans}} = 15.2\text{ Hz}$, CHN). ^{13}C NMR (CDCl_3 , 100 MHz) δ 117.9 (t, $^1J_{\text{CH}} = 163.2\text{ Hz}$, CH_2), 121.8 (d brd, $^1J_{\text{CH}} = 189.3\text{ Hz}$, CH), 128.3 (s brd, NCSe). ^{77}Se NMR (CDCl_3 , 76.3 MHz) δ -301 ppm . IR [ν (cm^{-1}), neat] 3115 (m, $\nu_{\text{C=CH}}$), 3055 (s, ν_{CH}), 2968 (m), 2119 (s, ν_{NCSe}), 1612 (s, $\nu_{\text{C=C}}$), 1394 (m), 1296 (m), 1132 (w), 940 (m), 906 (m).

Spectroscopic Experiments. The MW spectrum of vinyl isoselenocyanate was studied using the Stark-modulation MW spectrometer of the University of Oslo operating in the 7–120 GHz spectral range. Details of the construction and operation of this device have been given elsewhere.^{16–18} This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of $\sim 0.10\text{ MHz}$. Measurements were performed in the 11.5–77 GHz frequency interval. Radio-frequency microwave double-resonance (RFMWDR) experiments, similar to those performed by Wodarczyk and Wilson,¹⁹ were conducted to unambiguously assign particular transitions, using the equipment described elsewhere.¹⁶ The vapor pressure of the compound was found to be roughly 40 Pa at room temperature.

The spectra were recorded at room temperature or at about -5°C with pressures in the 5–10 Pa range and processed employing the Grams/AI program.²⁰

Quantum Chemical Methods. The present quantum chemical calculations were performed employing the Molpro²¹ and Gaussian 09²² suites of programs running on the Titan cluster in Oslo. Both *ab initio* and density functional theory (DFT) calculations were performed. Very high-level *ab initio* calculations were undertaken using coupled-cluster calculations with singlet and doublet excitation including noniterative triplet excitations, CCSD(T).²³ Coupled-cluster calculations with singlet and doublet excitations, CCSD,^{24–26} were also performed. Becke's three-parameter hybrid functional²⁷ employing the Lee, Yang, and Parr correlation functional, B3LYP,²⁸ and the M062X functional of Zhao and Truhlar²⁹ were employed in the DFT calculations. Peterson and Dunning's³⁰ correlation-consistent cc-pVTZ basis set, which is of triple- ζ quality, was chosen for these calculations. The frozen-core approximation was employed in the present calculations. The DFT calculations were performed with Gaussian 09, whereas Molpro was employed for the CCSD(T) calculations. CCSD calculations were performed using both of these computer programs.

RESULTS AND DISCUSSION

Quantum Chemical Calculations. B3LYP/cc-pVTZ calculations were first performed for **ap**. The structure, dipole moment, harmonic vibrational frequencies, and Watson's quartic centrifugal distortion constants³¹ were determined in this manner. The starting point in these calculations was the MP2/6-311++G** structure¹² of this conformer, which was assumed to be planar in the calculations, and all other structural parameters were varied freely. The calculations found **ap** to be a minimum ("stable" conformer), as all harmonic vibrational frequencies were positive. Selected results of these calculations are collected in Table 1S of the Supporting Information.

It is seen from this table that the important C2N3C4 angle is 152.8° and that the two lowest fundamental vibrations have values of 67 and 96 cm^{-1} . These modes are the in-plane and out-of-plane bending vibrations, respectively, of the isoselenocyanide group. Their comparatively low values are a manifestation of quasilinearity. Similar values for these two fundamentals were found in the MP2 calculations,¹² as well as in the M062X and CCSD(T) calculations below.

Attempts were next made to calculate the B3LYP structure of the hypothetical **sp** rotamer, employing the MP2 structure of this form¹² as the starting guess. Much to our surprise, these calculations did *not* converge to a stable **sp** conformer, but yielded **ap** instead. Attempts were then made to calculate the B3LYP rotational barrier about the C2N3 bond. We started from the **ap** form (C1C2N3C4 dihedral angle = 180°) and decreased this angle in steps of 10° , allowing all other structural parameters to vary freely. The geometry of the C2N3C4Se5 link of atoms was highly affected by this rotation, and it became increasingly linear as the C1C2N3C4 dihedral angle decreased. At a dihedral angle of 90° , this chain of atoms became completely linear. It was therefore not possible to obtain a barrier to internal rotation about the C2N3 bond using this method.

Another procedure was therefore undertaken in an attempt to determine whether the B3LYP method would be able to predict the stable existence of **sp**. Transformation from the **ap** rotamer to the hypothetical planar **sp** form can be achieved by

simply changing the C2N3C4 angle. A B3LYP potential function for this transformation was therefore calculated in an attempt to locate a second minimum that would correspond to **sp**. The B3LYP potential function was constructed for planar forms by calculating energies for fixed values of C2N3C4 between 130° and 220° allowing all remaining structural parameters to vary freely. A minimum in the potential function for a C2N3C4 angle less than 180° corresponds to an **ap** conformer, whereas a minimum for larger values than 180° of this angle would correspond to a **sp** rotamer. Steps sizes of 10° were used for the C2N3C4 angle. The resulting potential function is shown in Figure 1S in the Supporting Information. It is seen from this figure that there is only one minimum at 152.8° , namely, **ap**.

The fact that the MP2 and B3LYP calculations predict very different conformational properties for vinyl isoselenocyanate made it of interest to explore predictions of further quantum chemical methods, such as M062X, CCSD, and the very advanced CCSD(T) method. These three additional methods all predict that **ap** is the only stable form of the molecule. This result was obtained regardless of whether the MP2 structure of **ap** or **sp** was used as the starting point. CCSD calculations using Molpro and Gaussian yielded the same results, as expected.

Results of the M062X and CCSD calculations are summarized in Tables 2S and 3S, respectively, of the Supporting Information. Interestingly, the C2N3C4 angle of **ap** is predicted to be 170.0° in the M062X calculations (Table 2S, Supporting Information) and 164° in the CCSD calculations (Table 3S, Supporting Information).

The CCSD(T) method represents the highest quantum chemical level of theory explored in the present work. The CCSD(T) structure of **ap**, its dipole moment, and harmonic vibrational frequencies are collected in Table 1, where it is shown that the in-plane bending vibration of the isoselenocyanide group has a frequency of 70 cm^{-1} , whereas the out-of-plane bending fundamental has a frequency of 80 cm^{-1} .

Table 1. CCSD(T)/cc-pVTZ Structure,^a Rotational Constants, and Dipole Moment of the **ap Conformer of Vinyl Isoselenocyanate**

bond length (pm)		angle (deg)	
C1C2	133.8	C2C1H6	121.3
C1H6	108.1	C2C1H7	119.6
C1H7	108.0	H6C1H7	119.1
C2N3	138.7	C1C2N3	122.2
C2H8	108.4	C1C2H8	122.8
N3C4	119.4	N3C2H8	115.0
C4Se5	173.9	C2N3C4	151.0
		N3C4Se5	176.0 ^b
Rotational Constants ^c (MHz)			
A = 63678.9	B = 982.5	C = 967.5	
Dipole Moment ^{c,d} (10 ⁻³⁰ C m)			
μ _a = 11.99	μ _b = 2.14	μ _c = 0.0 ^e	μ _{tot} = 12.18
Vibrational Frequencies (cm ⁻¹)			
A' species: 3272, 3186, 3170, 2107, 1677, 1434, 1323, 1153, 989, 605, 420, 360, 70			
A'' species: 964, 912, 691, 408, 80			

^aAtom numbering given in Figure 1. Energy: $-6749063.44\text{ kJ/mol}$.

^bBent away from C1. ^cFor the $\text{H}_2\text{C}=\text{CHNC}^{30}\text{Se}$. ^dConversion factor: $1\text{ D} = 3.33564 \times 10^{-30}\text{ C m}$. ^eFor symmetry reasons.

Some of the structural parameters of Table 1 should be compared to relevant experimental findings. The C2N3C4 angle is predicted to be as large as 151° . This is similar to the values found for $\text{CH}_3\text{NCSe}^{10}$ and $\text{CH}_3\text{CH}_2\text{NCSe}^{11}$. π -electron conjugation of the vinyl and isoselenocyanide groups therefore seems to have a minor effect on the C2N3C4 angle.

Moreover, it is seen (Table 1) that the N3C4Se5 link of atoms is almost linear, as expected. The C1C2N3 angle takes a normal value of 122.2° for an sp^2 -hybridized carbon atom (C2). The C4Se5 bond length is 173.9 pm, 2.0 pm longer than determined for the corresponding bond in HNCSe (171.9 pm).¹ The C3N4 bond length of 119.4 pm is almost the same as its HNCSe counterpart (119.2 pm).¹ The C1C2 bond length of 133.8 pm should be compared to the r_z value [133.91(13) pm] of the CC bond length in ethylene.³² Conjugation of the π -electrons therefore seems to influence the double bond to a very small degree.

It is also of interest to compare the theoretical results, especially the CCSD(T) C2N3C4 angle, which is 13° smaller than the CCSD angle referred to above (164°) and as much as 19° smaller than the M062X angle (170°) but similar to the B3LYP angle (152.8°) and the MP2 angle (148.2°).¹² The large variation in this angle found in the two very high-level ab initio methods, CCSD and CCSD(T), is notable. Another important difference is found for the N3C4 bond length, whose CCSD(T) value is 119.4 pm (Table 1), compared to 117.6 pm for the CCSD calculations (Table 3S, Supporting Information). The remaining structural parameters of these two methods are similar. It is assumed that the significant structural differences predicted in the CCSD(T) and CCSD calculations again demonstrate the difficulties even these advanced methods encounter in dealing with the quasilinearity presented by this molecule.

A CCSD(T) potential function was calculated in a similar manner as reported above using the B3LYP method in another attempt to locate a second minimum that would correspond to **sp**. The present CCSD(T) function was constructed by calculating energies for fixed values of C2N3C4 between 130° and 216° allowing all remaining structural parameters to vary freely. Steps sizes as small as 2° or 3° were used for the C2N3C4 angle to avoid overlooking a possible stable **sp** form. The resulting potential function, which is somewhat similar to the B3LYP curve (Figure 1S, Supporting Information), is shown in Figure 2. This curve has only one minimum at 151° , namely, **ap**. The absence of a second minimum for C2N3C4 angles larger than 180° indicates that **sp** is not stable. The MP2 value of the C2N3C4 angle of **sp** is 211.8° ,¹² which lies in a region where the potential energy (Figure 2) is seen to be rather "flat" and to increase only slowly with increasing C2N3C4 angle.

The CCSD(T) potential function reveals another interesting feature, namely, that the energy varies by as little as about 4 kJ/mol for an 86° variation of the C2N3C4 angle. This means that a very floppy in-plane C2N3C4 bending vibration must exist for **ap**, which is, of course, consistent with quasilinearity of the isoselenocyanide group. Moreover, the nonsymmetrical shape of the curve indicates that this bending vibration is very anharmonic.

Only one of the theoretical methods, MP2/6-311++G**, indicates that **sp** exists, whereas this form could not be located in the CCSD(T), CCSD, B3LYP, and M062X calculations. However, the quantum chemical calculations for this compound are truly unusually demanding, and no safe

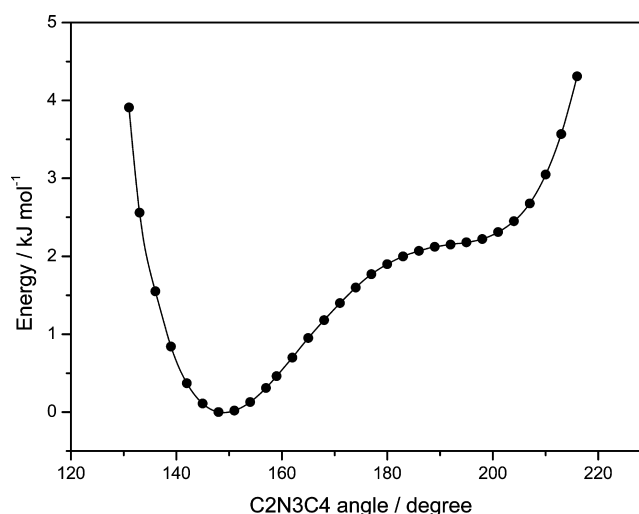


Figure 2. CCSD(T)/cc-pVTZ energy as a function of the C2N3C4 angle relative to the energy of the **ap** conformer, whose C2N3C4 angle is 151° (see text). The C1C2N3C4 dihedral angle is 180° .

conclusion could be reached from them whether **sp** indeed exists, because all of these methods have their shortcomings.

Microwave Spectrum. Because no definite conclusion regarding the conformational composition of vinyl isoselenocyanate could be reached from the quantum chemical calculations, a microwave investigation must take into account the possible existence of **sp** in addition to **ap**.

The CCSD(T) results in the preceding section were used to predict the spectrum of **ap**, whereas the MP2 predictions¹² were employed to search for the spectrum of **sp**. Ray's asymmetry parameter³³ κ was calculated to be about -0.9995 for **ap** and approximately -0.995 for **sp** from the relevant rotational constants. Both rotamers are therefore almost exactly symmetrical tops.

μ_a is the major dipole moment component, being roughly $(10\text{--}12) \times 10^{-30}$ C m in both **ap** and **sp**, according to the quantum chemical calculations. The MW spectra of both of these rotamers, which are near the prolate limit, should therefore be dominated by a -type R -branch pileups consisting of most of the K_{-1} transitions. The pileups are separated by the sum of B and C rotational constants ($B + C$). The near-degenerate $K_{-1} \geq 2$ lines have first-order, or nearly first-order, Stark effects, which lead to fully or nearly fully modulated spectra even at relatively low Stark fields.

Selenium has several naturally occurring isotopes. The most prominent of these are ^{80}Se (49.6%), ^{78}Se (23.8%), ^{76}Se (9.4%), and ^{82}Se (8.7%), where the percentage abundances are given in parentheses. Spectra of the isotopologues should be well-resolved from one another.

All of these features should lead to a spectrum consisting of densely populated intervals consisting of several isotopologues with their accompanying vibrationally excited states. There should be only a few lines between these dense intervals at low Stark fields. The separation between the intervals should be ~ 2.0 GHz for **ap**, corresponding to $B + C$ (Table 1), and approximately 2.2 GHz for **sp**, according to the MP2 predictions¹² for the sum of the corresponding two rotational constants.

Survey spectra observed at relatively low Stark fields revealed only *one* strong series of pileups separated by roughly 2.0 GHz, which strongly indicates that this series is the spectrum of **ap**.

There are very few transitions between pileup regions for relatively low values of J . However, the pileups broaden as J increases, resulting in absorption lines every few megahertz at high frequencies.

Most importantly, *no* similar series separated by approximately 2.2 GHz were observed. RFMWDR searches¹⁹ for several a -type R-branch transitions of spectrum of the hypothetical **sp** rotamer were conducted in rather large frequency intervals, but no signals compatible with this rotamer were observed. These searches were undertaken in regions where hundreds of transitions are observed in the Stark spectrum. The absence of a series characterized by $B + C \approx 2.2$ GHz and the failure to find **sp** by RFMWDR experiments are taken as experimental evidence that the energy difference between **ap** and **sp** must be considerably larger than about 2.4 kJ/mol predicted in the MP2 calculations,¹² if **sp** exists at all as a stable form of vinyl isoselenocyanate.

An illustration of a pileup region of **ap**, actually the $J = 8 \leftarrow 7$ region, is shown in Figure 3. A striking feature of this spectrum

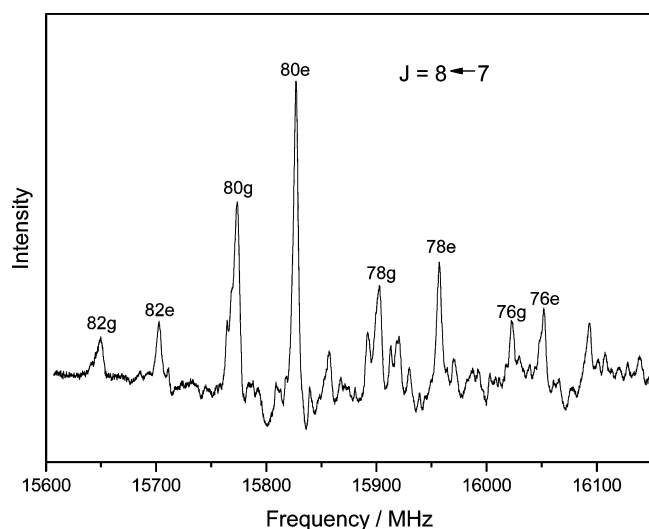


Figure 3. Survey spectrum taken at a Stark field strength of about 320 V/cm of the $J = 8 \leftarrow 7$ R-transition of $\text{H}_2\text{C}=\text{CHNCSe}$. The symbols above the peaks refer to the ground state, denoted **g**, and the first excited state (**e**) presumably of the lowest bending vibration. **80g** refers to the ground vibration of the ^{80}Se isotopologue, and **80e** refers to the first excited state of the lowest bending vibration of the same isotopologue, and so on. The absorption peaks of the four most abundant isotopologues are indicated. The ground and first excited states are spaced by $18(25) \text{ cm}^{-1}$. Note the different shapes of the pileups of ground and the first excited state, which are due to different centrifugal distortion constants, especially D_{JK} of the two states.

is the existence of *two* comparatively strong pileups for each isotopologue. One of them represents the ground vibrational state, and the other must be the first vibrationally excited state, presumably the lowest in-plane bending vibration. The values of the $B + C$ rotational constants of these two states are listed in Table 2. These entries were obtained from the pileup peaks of low- J transitions, where centrifugal distortion and asymmetry effects are relatively small. The changes in the rotational constants upon isotopic substitution from their ^{80}Se values were calculated from the CCSD(T) structure and used to make these assignments in a straightforward manner. The relative intensities observed for the various isotopologue pileups are

Table 2. Sum of the B and C Rotational Constants (MHz) of Vinyl Isoselenocyanate

	ground state	first excited state
$\text{H}_2\text{C}=\text{CHNC}^{76}\text{Se}$	2006.3(2)	2011.6(2)
$\text{H}_2\text{C}=\text{CHNC}^{77}\text{Se}$	1996.4(3)	2002.8(3)
$\text{H}_2\text{C}=\text{CHNC}^{78}\text{Se}$	1987.8(2)	1994.6(2)
$\text{H}_2\text{C}=\text{CHNC}^{80}\text{Se}$	1971.6(2)	1978.4(2)
$\text{H}_2\text{C}=\text{CHNC}^{82}\text{Se}$	1956.2(2)	1962.9(2)

consistent with the occurrence of the selenium isotope abundance referred to above.

It was not obvious from the intensities of the two strong pileups which of them represents the ground vibrational state and which is the first excited state. The fact that the centrifugal distortion effects are quite different for the two states (see below) complicated this identification. Relative intensity measurements had to be performed to settle this question. The pileups of low- J transitions were used for this purpose because centrifugal distortion effects are of less importance here than for high- J transitions, which reduces the complications originating from this effect. The integrated intensities of several pileups of the ^{80}Se isotopologue were obtained using the Grams/AI program. It was found that the high-frequency pileups had roughly 91% of the intensity of the low-frequency counterpart at -5°C . Assuming a Boltzmann distribution, $18(25) \text{ cm}^{-1}$ was obtained for the energy difference between the two states. The relatively large uncertainty illustrates that there is a small probability that the assignments of the ground and the first excited state should be reversed.

A harmonic bending vibration would lead to a succession of excited states separated by nearly constant frequency intervals and intensities diminishing by a factor of about 0.9 for each progressive excitation. This feature was *not* observed at all (see Figure 3). It is therefore concluded that the lowest bending vibration is highly anharmonic, and this is what one should expect from the potential curves shown in Figures 2 and 1S (Supporting Information).

However, there are additional much weaker excited states, found mostly on the high-frequency side of the ground-state pileups (Figure 3). The intensities of these excited states are less than about 25% of the intensity of the ground state at -5°C of the relevant isotopologue. No analyses of these states, which often overlap with the spectra of the isotopologues, were performed.

The different centrifugal distortion effects of the ground and excited bending vibrations can be seen both in Figure 3 and in Figure 4. This difference is mainly caused by the D_{JK} centrifugal distortion constant,³¹ which is responsible for the separation of the various K_{-1} states. This constant is quite different for the ground and vibrational excited states. It is seen in Figure 3 that the ground-state pileups are less symmetric and broader than the excited-state pileups. The broadening is caused by unresolved K_{-1} components. Centrifugal distortion becomes much more prominent as J increases. This is illustrated in Figure 4, where it is seen that the ground-state component of the $J = 17 \leftarrow 16$ transition is now split into well-resolved K_{-1} transitions, whereas the excited-state variant displays much smaller centrifugal distortion splittings.

Assignment of the Ground State. Individual K_{-1} lines must be assigned to determine all three rotational constants and centrifugal distortion constants. Asymmetry produces only well-separated $K_{-1} = 1$ lines because of the extreme prolateness of

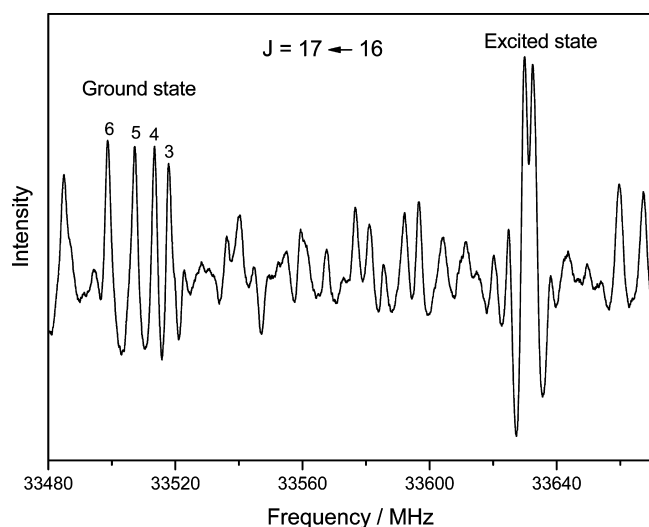


Figure 4. Spectrum of the $J = 17 \leftarrow 18$ transition of the ^{80}Se isotopologue taken at a Stark field strength of about 110 V/cm. The ground state has clearly resolved K_{-1} states, whose values are shown, whereas the first excited state of the bending vibration displays much less K_{-1} splitting. The $K_{-1} = 2$ and 0 states of the ground state, which both have frequencies near 33520 MHz, are not modulated at this field strength. The different behaviors of the two states are primarily due to different values of the D_{JK} centrifugal distortion constant.

this compound. $K_{-1} = 2$ lines also split up for high values of J . The last-mentioned transitions were first assigned unambiguously using the RFMWDR technique. The frequencies of the $K_{-1} = 1$ lines could then be predicted quite accurately, and they were readily assigned. The prominent centrifugal distortion splitting into individual K_{-1} lines (see Figure 4) greatly facilitated the assignments of the K_{-1} lines in the 3–6 range.

The transitions assigned in this manner were fitted to Watson's S reduction I^r representation³¹ Hamiltonian using Sørensen's program Rotfit.³⁴ The rotational constants, two quartic, D_J and D_{JK} , and two sextic, H_{JK} and H_{KJ} , centrifugal distortion constants, were least-squares-fitted for the ^{80}Se variant. All remaining centrifugal distortion constants were preset at zero. Inclusion of additional centrifugal distortion constants was tested, but significant values were not obtained for them. Attempts to include lines with $K_{-1} \geq 7$ produced much poorer fits to the Watson Hamiltonian. It is assumed that this is due to higher-order vibration–rotation effects. The spectrum of the parent species consisting of 227 transitions with $J_{\text{max}} = 38$ is listed in Table S5 of the Supporting Information, and the resulting spectroscopic constants are listed in Table 3.

It is seen from this table that the B and C rotational constants were accurately determined, whereas A has an extremely large uncertainty and is essentially indeterminate. This is because only aR transitions were assigned for this extremely prolate asymmetrical top. A much more accurate value of the A rotational constants would have been obtained if b -type transitions were available. However, no such lines were identified, presumably because of a relatively small μ_b value, whose CCSD(T) value is $\sim 2 \times 10^{-30}$ C m (Table 1), producing insufficient intensities for b -type lines.

The spectrum of the ^{78}Se isotopologue was assigned in the same manner as the described for the parent species. A total of 132 transitions are listed in Table 4S in the Supporting Information, and the spectroscopic constants are reported in

Table 3. Spectroscopic Constants^{a–c} of the Ground State of Isoselenocyanate

	species	
	$\text{H}_2\text{C}=\text{CHNC}^{78}\text{Se}$	$\text{H}_2\text{C}=\text{CHNC}^{80}\text{Se}$
A (GHz)	57.4 ^d	57.4(20)
B (MHz)	1002.213(14)	993.9244(42)
C (MHz)	985.907(15)	978.0141(34)
κ^e	−0.9994219(10)	−0.999436(20)
D_J (kHz)	0.03772(42)	0.03697(97)
D_{JK} (kHz)	14.049(29)	13.84(11)
H_{JK} (Hz)	0.2745 ^d	0.275(33)
H_{KJ} (Hz)	−159.7 ^d	−159.7(25)
Δ^f (10^{-20} u m ²)	−0.46(1)	−0.53(30)
rms ^g	1.55	1.35
no. of transitions ^h	132	227

^a S reduction, I^r representation. ^bSpectra are listed in the Supporting Information, Tables 4S and 5S. ^cUncertainties represent one standard deviation. ^dFixed. ^eRay's asymmetry parameter.³³ ^fInertial defect. ^gRoot-mean-square deviation. ^hNumber of transitions used in the least-squares fit.

Table 3. The A rotational constant and the H_{JK} and H_{KJ} sextic centrifugal distortion constants were preset to the values for the ^{80}Se variant in the least-squares fit.

Comparison of the experimental (Table 3) and CCSD(T) B and C rotational constants (Table 1) is in order. It is seen that the experimental constants of the ^{80}Se isotopologue are about 1% larger than the theoretical constants. A difference of this magnitude is not surprising, because of the different natures of the rotational constants. The CCSD(T) rotational constants reflect an approximate equilibrium, r_e , structure, whereas the experimental constants reflect an effective, r_0 , structure.

The substitution coordinates³⁵ were calculated for the selenium atom using the entries of Table 3 in Kraitichman's equations.³⁶ The a -axis coordinate was found to be $|a| = 143.2(2)$ pm. The uncertainty, ± 0.2 pm, was obtained using van Eijck's prescription.³⁷ The b -axis coordinate of this atom was found to be very small and so uncertain that it is not worth quoting. The CCSD(T) coordinate is $|a| = 144.8$ pm.

Assignment of the First Excited State of the Lowest Bending Vibration. The assignment of the spectrum of the ^{80}Se isotopologue was made in a manner analogous to that reported above for the ground-state spectrum. No lines with $K_{-1} \geq 6$ were employed for similar reasons as described in the previous section. A total of 145 transitions with $J_{\text{max}} = 32$, which are listed in Table 7S of the Supporting Information, were used to determine the spectroscopic constants displayed in Table 4. It is seen that the A rotational constant is practically indeterminate.

The corresponding spectrum of the ^{78}Se species (100 transitions) is listed in Table 6S (Supporting Information). The A rotational constants and the centrifugal distortion constants were preset at the values found for the parent species in the least-squares fit with the results shown in Table 4.

The D_{JK} centrifugal distortion constant of this excited state (Table 4) has the opposite sign and an absolute value that is much smaller than that of the ground state (Table 3). There is also a comparatively large difference in D_J for the two states. The strikingly different quartic centrifugal distortion constants of the ground and first excited states are another manifestation of a significant vibration–rotation interaction.

Table 4. Spectroscopic Constants^{a–c} of the First Excited State of Isoselenocyanate

	species	
	H ₂ C=CHNC ⁷⁸ Se	H ₂ C=CHNC ⁸⁰ Se
A (GHz)	46.9 ^d	46.9(25)
B (MHz)	1004.82(16)	997.0589(58)
C (MHz)	989.85(16)	981.3627(34)
κ ^e	−0.999348(14)	−0.99932(4)
D _J (kHz)	0.0267 ^d	0.0267(22)
D _{JK} (kHz)	−0.62 ^d	−0.62(24)
H _{JK} (Hz)	−0.455 ^d	−0.455(96)
H _{KJ} (Hz)	−378.8 ^d	−378.8(74)
Δ ^f (10 ^{−20} u m ²)	−3.2(2)	−2.7(6)
rms ^g	1.82	1.31
no. of transitions ^h	100	145

^aS reduction, ^f representation. ^bSpectra are listed in the Supporting Information, Tables 6S and 7S. ^cUncertainties represent one standard deviation. ^dFixed. ^eRay's asymmetry parameter.³³ ^fInertial defect. ^gRoot-mean-square deviation. ^hNumber of transitions used in the least-squares fit.

CONCLUSIONS

It has been assumed that the gas phase of each member of the isocyanate series H₂C=CHNCX, where X = O, S, or Se, would consist of a mixture of a CCNC synperiplanar and an antiperiplanar conformer. This is indeed the case for H₂C=CHNCO,¹³ whereas only the antiperiplanar form was found for H₂C=CHNCS.¹⁴ It is uncertain whether a synperiplanar form exists for this compound.¹⁴ Low-frequency vibrations are prominent features of the MW spectra of the oxygen¹³ and sulfur analogues¹⁴ of vinyl isoselenocyanate.

However, the present study shows that nonrigidity is much more prominent in H₂C=CHNCSe than in its oxygen and sulfur congeners. For example, the lowest vibrational frequency of antiperiplanar H₂C=CHNCS is 130(30) cm^{−1},¹⁴ compared to 18(25) cm^{−1} in H₂C=CHNCSe. The substitution of a sulfur atom with a selenium atom thus has a dramatic effect on the vibrational properties. The lowest bending vibration of the title compound is extremely low [18(25) cm^{−1}] and strongly anharmonic. The centrifugal distortion constants, especially D_{JK} (Tables 3 and 4), of the two states show extreme variation. All of these characteristics are typical of quasilinearity.

Five different quantum chemical methodologies, namely, MP2, CCSD(T), CCSD, B3LYP, and M062X, were employed to investigate the conformational and dynamical properties of the title compound. Only MP2 predicts the existence of a synperiplanar form,¹² whereas the other four methods do not indicate the stable coexistence of this rotamer. There is no evidence in the MW spectrum for the existence of the synperiplanar form, which must have a relatively high energy, if it exists at all.

The equilibrium values of the CNC angle of H₂C=CHNCSe describe the deviation from nonlinearity. This angle, which varies from 151° to 170° in the antiperiplanar conformer in the various quantum chemical methods employed (see above), would be 180° if the isoselenocyanide group were completely linear. However, the large-amplitude in-plane bending vibration [18(25) cm^{−1}] suggests that this compound should rather be regarded as having a quasilinear CNCSe link of atoms than a rigid and bent antiperiplanar form.

ASSOCIATED CONTENT

Supporting Information

Results of the theoretical calculations and the microwave spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*Tel.: +47 2285 5674. Fax: +47 2285 5441. E-mail: harald.mollendal@kjemi.uio.no (H.M.).

*E-mail: jean-claude.guillemin@ensc-rennes.fr (J.-C.G.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Anne Horn for her skillful assistance. The Research Council of Norway (Program for Supercomputing) is thanked for a grant of computer time. J.-C. G. thanks the CNES for financial support.

REFERENCES

- (1) Vogt, J.; Winnewisser, M. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 444.
- (2) Vogt, J.; Winnewisser, M. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 439.
- (3) Vogt, J.; Winnewisser, M. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 439.
- (4) Yamada, K.; Winnewisser, M. *Z. Naturforsch. A* **1976**, *31A*, 139.
- (5) Bunker, P. R.; Howe, D. J. *J. Mol. Spectrosc.* **1980**, *83*, 288.
- (6) Koput, J. *J. Mol. Spectrosc.* **1986**, *118*, 448.
- (7) Koput, J.; Stroth, F.; Winnewisser, M. *J. Mol. Spectrosc.* **1990**, *140*, 31.
- (8) Koput, J.; Krüger, M.; Dreizler, H. *J. Mol. Spectrosc.* **1992**, *151*, 260.
- (9) Franklin, W. J.; Werner, R. L.; Ashby, R. A. *Spectrochim. Acta A* **1974**, *30A*, 1293.
- (10) Sakaizumi, T.; Yasukawa, A.; Miyamoto, H.; Ohashi, O.; Yamaguchi, I. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1614.
- (11) Sakaizumi, T.; Iida, K.; Ohashi, O.; Yamaguchi, I. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1991.
- (12) Badawi, H. M.; Forner, W.; Seddigi, Z. S. *J. Mol. Struct. (THEOCHEM)* **2003**, *631*, 127.
- (13) Kirby, C.; Kroto, H. W. *J. Mol. Spectrosc.* **1978**, *70*, 216.
- (14) Caminati, W. *J. Mol. Struct.* **1988**, *190*, 227.
- (15) Chrostowska, A.; Matrane, A.; Maki, D.; Khayar, S.; Ushiki, H.; Gracia, A.; Belachemi, L.; Guillemin, J.-C. *ChemPhysChem* **2012**, *13*, 226.
- (16) Møllendal, H.; Leonov, A.; de Meijere, A. *J. Phys. Chem. A* **2005**, *109*, 6344.
- (17) Møllendal, H.; Cole, G. C.; Guillemin, J.-C. *J. Phys. Chem. A* **2006**, *110*, 921.
- (18) Samdal, S.; Møllendal, H.; Hnyk, D.; Holub, J. *J. Phys. Chem. A* **2011**, *115*, 3380.
- (19) Wodarczyk, F. J.; Wilson, E. B., Jr. *J. Mol. Spectrosc.* **1971**, *37*, 445.
- (20) GRAMS/AI, 7th ed.; Thermo Scientific: Waltham, MA, 2002.
- (21) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Berning, A. A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Koeppl, C.; Liu, Y.; Lloyd, A. W.; Palmieri, R. P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *Molpro*, version 2010.1; University College Cardiff Consultants Limited: Cardiff, U.K., 2010. Accessed January 2012. Available at <http://www.molpro.net/>.

- (22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, R.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision B.01; Gaussian, Inc: Wallingford, CT, 2010.
- (23) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, 227, 321.
- (24) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, 76, 1910.
- (25) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, 89, 7382.
- (26) Hampel, C.; Peterson, K. A.; Werner, H. J. *Chem. Phys. Lett.* **1992**, 190, 1.
- (27) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098.
- (28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (29) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, 120, 215.
- (30) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, 117, 10548.
- (31) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6.
- (32) Hirota, E.; Endo, Y.; Saito, S.; Yoshida, K.; Yamaguchi, I.; Machida, K. *J. Mol. Spectrosc.* **1981**, 89, 223.
- (33) Ray, B. S. *Z. Phys.* **1932**, 78, 74.
- (34) Sørensen, G. O. *J. Mol. Spectrosc.* **1967**, 22, 325.
- (35) Costain, C. C. *J. Chem. Phys.* **1958**, 29, 864.
- (36) Kraitchman, J. *Am. J. Phys.* **1953**, 21, 17.
- (37) Van Eijck, B. P. *J. Mol. Spectrosc.* **1982**, 91, 348.