Millimeter Wave Spectrum and Structure of Isoselenocyanic Acid, HNCSe

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The rotational a-type spectra of the five most abundant isotopomers of HNCSe were recorded in natural abundance. Using Watson's S-reduced Hamiltonian the rotational and some centrifugal distortion constants could be determined for the ground vibrational state of the various isotopic species. With the aid of these constants the r_s -structure of HNCSe could be refined and the parameter specifying the quasilinearity of the molecule could be estimated.

1. Introduction

From a chemical point of view isoselenocyanic acid, HNCSe, belongs to the interesting group of homologs of isocyanic acid, HNCO. Recently the existence of HNCSe in the gaseous phase has been demonstrated by the detection of its microwave spectrum in our laboratory [1]. In the preceeding paper [2] we have reported an improvement of the preparation of this rather unstable molecule, which decays in the gaseous phase according to a reaction of second order. Moreover we have characterized this molecule by its infrared spectra in the gaseous phase and in an argon matrix.

Like HNCO and HNCS, HNCSe belongs to a group of quasilinear molecules whose dynamics have been intensively studied by spectroscopists and theorists. A bent polyatomic molecule with N atoms possesses $3N-6$ vibrational degrees of freedom, which can normally be separated from the three rotational degrees of freedom since the vibrational energy quanta are much larger than the rotational quanta. In a linear molecule $3N-5$ vibrational degrees of freedom and two rotational degrees of freedom may be defined. However, in a number of molecules this separation of variables according to the Born-Oppenheimer approximation breaks down and one degree of freedom cannot be classified as clearly vibrational or rotational, leading to a quasilinear molecule which is between a linear and a bent model. The treatment of such a species follows in analogy with that of asymmetric tops: A prolate symmetric top can be transformed into an oblate top via the asymmetric top by varying the geometry; a linear molecule can be converted into a slightly asymmetric top, thereby converting a vibrational degree of freedom into a rotational degree of freedom, by varying the bending potential function. Between the two limiting cases is the region of the quasilinear molecules, characterized by a large-amplitude bending vibration.

A simple parameter which quantifies quasilinearity is derived on the basis of the separation of variables in the Born-Oppenheimer approximation [3]. The quasilinearity parameter γ is defined by

$$\gamma = \frac{E(\text{lowest state with } K \text{ or } l = 1)}{E(\text{lowest excited state with } K \text{ or } l = 0)} \quad (1)$$

Hereby the energies E are referred to the lowest-lying energy level. In the case of the bent molecule, where these rotational

and vibrational energies are well separated, the parameter γ is of the order of 10^{-2} , which is given by the square of the Born-Oppenheimer constant. In the case of a linear molecule with a two-dimensional isotropic harmonic oscillator this parameter is 0.5. In analogy with Ray's asymmetry parameter κ , which runs from -1 to $+1$, the quasilinearity parameter is redefined by

$$\gamma_0 = 1 - 4\gamma \quad (2)$$

Therefore, the bent limiting case is described by $\gamma_0 = +1$ and the linear limiting case by $\gamma_0 = -1$ [3]. However, this parameter, which can be applied in rovibrational Hamiltonians of quasilinear molecules, has been recently extended in range to -3 for describing polytopic molecules such as KCN and LiCN, in which a free rotation takes place [4].

Quasilinear molecules exhibit extreme centrifugal distortion behaviour. Moreover, it can happen via Coriolis interactions that the energy levels of other bending modes are seriously affected. For example in isocyanic acid, HNCO, and isothiocyanic acid, HNCS, there are strong Coriolis resonances connecting the quasilinear in-plane bending mode ν_4 and the in-plane and out-of-plane bending modes ν_5 and ν_6 , respectively. In the case of HNCO the $K_a = 1$ substate of $\nu_5 = 1$ is dramatically lowered with respect to the $K_a = 0$ substate by these resonances [5], whereas in HNCS these substates are even inverted [6]. Therefore HNCSe was chosen in order to contribute further to understanding of the dynamics of quasilinear molecules.

2. Rotational Spectrum of HNCSe

Due to the isotopic distribution of selenium, the HNCSe spectrum shows obvious isotopic patterns. A list of the most abundant isotopomers of HNCSe is given in Table 1. As in the pseudohalogen hydrides HN₃ [7], HNCO [8] and HNCS [9] the dipole moment vector

Table 1
Relative isotopic abundances of isoselenocyanic acid, HNCSe

Isotopomer	Relative abundance/%
H ¹⁴ N ¹² C ⁸² Se	9.1
H ¹⁴ N ¹² C ⁸⁰ Se	49.8
H ¹⁴ N ¹² C ⁷⁸ Se	23.5
H ¹⁴ N ¹² C ⁷⁷ Se	7.5
H ¹⁴ N ¹² C ⁷⁶ Se	9.0
H ¹⁴ N ¹² C ⁷⁴ Se	0.8
H ¹⁴ N ¹³ C ⁸⁰ Se	0.5
H ¹⁵ N ¹² C ⁸⁰ Se	0.2

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Fig. 1

HNCSe structure drawn in the principal axis system with the orientation of the dipole moment components. Only the component of the dipole moment along the *a*-axis has been measured (Ref. [1]). The total dipole moment was assumed to be parallel to the NH bond

in isoselenocyanic acid, HNCSe, should be approximately parallel to the NH bond, as is shown in Fig. 1. Since the total dipole moment has components along the principal axes of the inertia tensor, there are components along both the *a*- and *b*-axes. Landsberg [1] determined the electric dipole moment component μ_a to be 1.98 D by Stark effect measurements. The component μ_b should be in the order of 1 D under the assumption mentioned above and with the structure shown here. This implies that *a*- and *b*-type rotational spectra can be expected.

Assuming the slightly bent structure shown in Fig. 1, based on Landsberg's structural parameters [1], the rotational constant *A* can be estimated to be 1.7 THz. That means that the *b*-type Q-branches should start at *A*, which is about 56.7 cm^{-1} , and continue with a separation of $2A$. Thus, the large *A*-rotational constant makes the prediction of the microwave and millimeter wave *b*-type spectrum extremely difficult, which should be most accessible in the far infrared region. Unfortunately we failed in detecting the rotational *b*-type spectrum in the far-infrared region using a broad-band Fourier transform spectrometer (Digilab FTS 20B) due to the limited resolution and sensitivity of the interferometer and due to the limited lifetime of the molecule.

Since the sensitivity and the resolution of our millimeter wave spectrometer is much higher than that of our interferometer, it was possible to observe the rotational *a*-type spectrum. The experimental setup of the millimeter wave spectrometer employed in this study is

Fig. 2

Fortrat diagram of the observed *a*-type rotational transitions of $\text{H}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$. There are similar diagrams for the less abundant isotopomers

described elsewhere [10–12]. A free space glass cell with a length of 2.60 m was used. The cell was conditioned by HNCSe and filled with HNCSe to a total pressure of about 2.5 Pa. No carrier gas was needed.

The *a*-type rotational transitions of the R-branch were measured up to 225 GHz for the five most abundant isotopomers of HNCSe in natural abundance. In Fig. 2 a Fortrat diagram is shown for the main isotopic species $\text{H}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$. The rotational quantum number *J* of the lower level is plotted versus the experimental effective rotational constant B_{eff} , obtained by dividing the observed frequency of the *a*-type R-branch transition by $2(J+1)$. The same spectral pattern or part of it can be observed for the other isotopic species, whose transitions are well separated from the lines of the main isotopic species.

The rotational transitions could be assigned up to $K_a = 3$ in the ground vibrational state. This assignment was derived from the intensity of the lines and by the comparison of the K_a patterns of the R-branch transitions in HNCSe, HNCSe and HNCSe. In contrast to HNCSe and HNCSe the $K_a = 2$ transitions are not split by the asymmetry of the molecule even at *J* as high as 27. That means that the molecule indeed has an extremely large rotational constant *A*. The points in the Fortrat diagram which are not connected by curves describe rotational transitions arising from HNCSe molecules in excited states of the bending modes. We have not yet been able to assign them.

For the numerical analysis of the assigned transitions Watson's S-reduced Hamiltonian [13] was applied. In order to describe properly the observed spectra of HNCSe and HNCSe, which exhibit extremely large centrifugal distortion effects, Yamada [14] added higher order distortion terms to the Hamiltonian. This Hamiltonian has the following form

$$\begin{aligned} \hat{H} = & (A - \frac{1}{2}(B+C))\hat{P}_z^2 + \frac{1}{2}(B+C)\hat{P}^2 \\ & - D_J\hat{P}^4 - D_{JK}\hat{P}^2\hat{P}_z^2 - D_K\hat{P}_z^4 \\ & + H_{JK}\hat{P}^4\hat{P}_z^2 + H_{KJ}\hat{P}^2\hat{P}_z^4 + H_K\hat{P}_z^6 \\ & - L_{JK}\hat{P}^4\hat{P}_z^4 - L_{KJ}\hat{P}^2\hat{P}_z^6 - L_K\hat{P}_z^8 \\ & + S_{KJ}\hat{P}^2\hat{P}_z^8 + S_K\hat{P}_z^{10} \\ & - T_{KJ}\hat{P}^2\hat{P}_z^{10} - T_K\hat{P}_z^{12} + U_K\hat{P}_z^{14} \\ & + (\frac{1}{4}(B-C) + d_1\hat{P}^2)(\hat{P}_+^2 + \hat{P}_-^2) + d_2(\hat{P}_+^4 + \hat{P}_-^4) \\ \hat{P}_{\pm} = & \hat{P}_x \pm i\hat{P}_y \end{aligned} \quad (3)$$

where $\hat{P}$, $\hat{P}_x$, $\hat{P}_y$, and $\hat{P}_z$ are the operators for the total angular momentum and its components, respectively. The coefficients *A*, *B* and *C* are Watson's reduced rotational constants in the I' axis representation. D_J , D_{JK} , D_K , d_1 and d_2 are quartic centrifugal distortion constants, whereas H_{JK} , H_{KJ} and H_K are sextic distortion constants. The remaining coefficients are higher order distortion constants.

Using this Hamiltonian the rotational and centrifugal distortion constants were determined. Since the $K_a = 2$ transitions are not split by the inertial asymmetry of the molecule even at *J* = 27 and no *b*-type spectrum could be measured, the rotational constant *A* could not be determined. Consequently this rotational constant was assumed to be 1.7 THz for all observed isotopomers and was held fixed during the least squares analysis. The $K_a = 2$ transitions were therefore weighted by a factor of 0.5, whereas the microwave data [1], which have been included in these fits, were weighted with 0.1 or 0.05 because of the unresolved nuclear quadrupole hyperfine structure. All other lines were given unit weight. In Tables 2–6 the observed and calculated rotational *a*-type transitions of the five most abundant isotopomers of HNCSe are listed for the ground vibrational state.

The resulting spectroscopic constants and the corresponding correlation matrix are given in Tables 7a and b. With increasing selenium mass the rotational constants *B* and *C* decrease as expected. The quartic centrifugal distortion constants D_J follow *B* and *C*, whereas D_{JK} increases. The same behaviour can be seen for the sextic centrifugal distortion constant H_{KJ} . The distortion constants d_1 and d_2 are insensitive to isotopic substitution of selenium. Since only *a*-type transitions were observed, the constants D_K and H_K could not be determined and were held fixed at zero. As no $K_a = 3$ lines could be detected for the less abundant isotopomers, no octic centrifugal

Table 2

Observed and calculated rotational transitions in MHz of $H^{14}N^{12}C^{82}Se$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs.	calc.	obs-calc
2(0, 2) - 1(0, 1)	15644.3900	15644.3739	0.0161 a
2(1, 2) - 1(1, 1)	15637.5400	15637.4097	0.1303 a
2(1, 1) - 1(1, 0)	15668.1600	15668.2130	-0.0530 a, b
3(0, 3) - 2(0, 2)	23466.5300	23466.5227	0.0073 a
3(1, 3) - 2(1, 2)	23456.1400	23456.0770	0.0630 a
3(1, 2) - 2(1, 1)	23502.2600	23502.2814	-0.0214 a
3(2, 2) - 2(2, 1)	23493.1000	23493.0346	0.0654 a
3(2, 1) - 2(2, 0)	23493.1000	23493.0346	0.0654 a
14(0, 14) - 13(0, 13)	109503.7690	109503.7739	-0.0049
14(1, 14) - 13(1, 13)	109455.1450	109455.1521	-0.0071
14(1, 13) - 13(1, 12)	109670.6760	109670.6676	0.0084
14(2, 13) - 13(2, 12)	109627.6080	109627.6142	-0.0062
14(2, 12) - 13(2, 11)	109627.6080	109627.6142	-0.0062
18(0, 18) - 17(0, 17)	140784.7070	140784.7004	0.0066
18(1, 18) - 17(1, 17)	140722.2870	140722.2966	-0.0096
18(1, 17) - 17(1, 16)	140999.2980	140999.2958	0.0022
18(2, 17) - 17(2, 16)	140944.0320	140944.0277	0.0043
18(2, 16) - 17(2, 15)	140944.0320	140944.0278	0.0042
19(0, 19) - 18(0, 18)	148604.2940	148604.2829	0.0111
19(1, 19) - 18(1, 18)	148538.4480	148538.4457	0.0023
19(1, 18) - 18(1, 17)	148830.7830	148830.8056	-0.0226
19(2, 18) - 18(2, 17)	148772.5040	148772.4934	0.0106
19(2, 17) - 18(2, 16)	148772.5040	148772.4934	0.0106
22(0, 22) - 21(0, 21)	172061.2400	172061.2276	0.0124
22(1, 22) - 21(1, 21)	171985.1270	171985.1240	0.0030
22(1, 21) - 21(1, 20)	172323.5370	172323.5378	-0.0008
22(2, 21) - 21(2, 20)	172256.1060	172256.1198	-0.0138
22(2, 20) - 21(2, 19)	172256.1060	172256.1198	-0.0138
23(0, 23) - 22(0, 22)	179879.5340	179879.5574	-0.0234
23(1, 23) - 22(1, 22)	179800.0490	179800.0439	0.0051
23(1, 22) - 22(1, 21)	180153.8120	180153.7987	0.0133
23(2, 22) - 22(2, 21)	180083.3590	180083.3550	-0.0040
23(2, 21) - 22(2, 20)	180083.3590	180083.3550	-0.0040

a Ref. (1)

b corrected value

distortion constants could be obtained. Thus the values of L_{JK} and L_{KJ} were taken from the main isotopic species and held fixed during the least squares analysis. The standard deviations σ of these fits were between 14 and 20 kHz.

Fig. 3

Comparison of the scaled spectral stick pattern of a-type rotational transitions in the R-branches in isocyanic acid homologs HNCX. The asymmetry splittings of the $K_a = 1$ doublets are normalized

Table 3

Observed and calculated rotational transitions in MHz of $H^{14}N^{12}C^{80}Se$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs.	calc.	obs-calc
2(0, 2) - 1(0, 1)	15733.0000	15732.9861	0.0139 a
2(1, 2) - 1(1, 1)	15725.9900	15725.8887	0.1013 a
2(1, 1) - 1(1, 0)	15757.0200	15757.0399	-0.0199 a
3(0, 3) - 2(0, 2)	23599.4500	23599.4405	0.0095 a
3(1, 3) - 2(1, 2)	23588.8200	23588.7952	0.0248 a
3(1, 2) - 2(1, 1)	23635.5100	23635.5214	-0.0114 a
3(2, 2) - 2(2, 1)	23626.1400	23626.0668	0.0732 a
3(2, 1) - 2(2, 0)	23626.1400	23626.0668	0.0732 a
13(0, 13) - 12(0, 12)	102258.9000	102258.8848	0.0152
13(1, 13) - 12(1, 12)	102212.8510	102212.8588	-0.0078
13(1, 12) - 12(1, 11)	102415.2570	102415.2561	0.0009
13(2, 12) - 12(2, 11)	102374.3920	102374.3774	0.0146
13(2, 11) - 12(2, 10)	102374.3920	102374.3775	0.0145
13(3, 10) - 12(3, 9)	102215.9600	102215.9667	-0.0067
14(0, 14) - 13(0, 13)	110123.9920	110123.9792	0.0128
14(1, 14) - 13(1, 13)	110074.4300	110074.4316	-0.0016
14(1, 13) - 13(1, 12)	110292.3700	110292.3830	-0.0130
14(2, 13) - 13(2, 12)	110248.3800	110248.3763	0.0037
14(2, 12) - 13(2, 11)	110248.3800	110248.3764	0.0036
14(3, 11) - 13(3, 10)	110077.7530	110077.7415	0.0115
18(0, 18) - 17(0, 17)	141582.0520	141582.0388	0.0132
18(1, 18) - 17(1, 17)	141518.4360	141518.4498	-0.0138
18(1, 17) - 17(1, 16)	141798.5690	141798.5812	-0.0122
18(2, 17) - 17(2, 16)	141742.1110	141742.1022	0.0088
18(2, 16) - 17(2, 15)	141742.1110	141742.1024	0.0086
18(3, 15) - 17(3, 14)	141522.4720	141522.4793	-0.0073
19(0, 19) - 18(0, 18)	149445.9010	149445.8970	0.0040
19(1, 19) - 18(1, 18)	149378.7890	149378.8102	-0.0212
19(1, 18) - 18(1, 17)	149674.4570	149674.4766	-0.0196
19(2, 18) - 18(2, 17)	149614.8750	149614.8906	-0.0156
19(2, 17) - 18(2, 16)	149614.8750	149614.8908	-0.0158
19(3, 16) - 18(3, 15)	149382.9830	149382.9946	-0.0116
22(0, 22) - 21(0, 21)	173035.6560	173035.6477	0.0083
22(1, 22) - 21(1, 21)	172958.1020	172958.1033	-0.0013
22(1, 21) - 21(1, 20)	173300.3520	173300.3462	0.0058
22(2, 21) - 21(2, 20)	173231.4830	173231.4705	0.0125
22(2, 20) - 21(2, 19)	173231.4830	173231.4707	0.0123
22(3, 19) - 21(3, 18)	172962.6840	172962.6828	0.0012
23(0, 23) - 22(0, 22)	180898.2420	180898.2386	0.0034
23(1, 23) - 22(1, 22)	180817.2270	180817.2210	0.0060
23(1, 22) - 22(1, 21)	181174.9820	181174.9792	0.0028
23(2, 22) - 22(2, 21)	181103.0300	181103.0183	0.0117
23(2, 21) - 22(2, 20)	181103.0300	181103.0184	0.0116
23(3, 20) - 22(3, 19)	180821.9180	180821.9071	0.0109
24(0, 24) - 23(0, 23)	188760.4710	188760.4741	-0.0031
24(1, 23) - 23(1, 22)	189049.2560	189049.2583	-0.0023
27(0, 27) - 26(0, 26)	212344.8760	212344.8934	-0.0174
27(1, 27) - 26(1, 26)	212250.0600	212250.0548	0.0052
27(1, 26) - 26(1, 25)	212669.8280	212669.8171	0.0109
27(2, 26) - 26(2, 25)	212585.5670	212585.5779	-0.0109
27(2, 25) - 26(2, 24)	212585.5670	212585.5778	-0.0108
28(0, 28) - 27(0, 27)	220205.5380	220205.5526	-0.0146
28(1, 28) - 27(1, 27)	220107.2960	220107.2782	0.0178
28(1, 27) - 27(1, 26)	220542.5380	220542.5260	0.0120
28(2, 27) - 27(2, 26)	220455.2210	220455.2343	-0.0133
28(2, 26) - 27(2, 25)	220455.2210	220455.2341	-0.0131

a Ref. (1)

It is obvious that the rotational and centrifugal distortion constants in Table 7 constitute fitting parameters. Normally the quadratic, quartic and sextic constants differ successively by about four orders of magnitude. The breakdown of the Born-Oppenheimer approximation, which is characteristic for quasilinear behaviour, can thus be seen in the extreme centrifugal distortion. In Table 8 the molecular parameters of HNCSe are compared with those HNC and HNCS. Hereby rotational transitions have been taken into account up to $K_a = 6$ for HNC [14], $K_a = 4$ for HNCS [15] and $K_a = 3$ for HNCSe.

Comparing the rotational constants of HNC, HNCS and HNCSe we see that the constant A increases, whereas the constants B and C decrease. This is due not only to the increasing mass of the chalcogen, but also to an enlargement of the average HNC angle (see below). An analogous decrease is observed for the quartic centrifugal distortion constants D_J , D_{JK} , d_1 and d_2 . Due to the change of the sign of D_{JK} from HNC to HNCS the spectral pattern of the a-type rotational transitions in the R-branch is altered significantly, as is shown in Fig. 3. In this case the positions of the higher K_a lines are shifted to higher frequencies with respect to $K_a = 0$. Because of the strong decrease of the sextic centrifugal distortion constant H_{KJ} in HNCSe the $K_a = 3$ lines are shifted again to lower frequencies. Rotational transitions for $K_a = 4$ were not observed due to the unfavourable Boltzmann distribu-

Table 4

Observed and calculated rotational transitions in MHz of $\text{H}^{14}\text{N}^{12}\text{C}^{78}\text{Se}$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs.	calc.	obs-calc
2(0, 2) - 1(0, 1)	15826.0100	15825.9967	0.0133 a
2(1, 2) - 1(1, 1)	15818.8800	15818.7580	0.1220 a
2(1, 1) - 1(1, 0)	15850.2300	15850.2779	-0.0479 a
3(0, 3) - 2(0, 2)	23738.9700	23738.9559	0.0141 a
3(1, 3) - 2(1, 2)	23728.1300	23728.0987	0.0313 a
3(1, 2) - 2(1, 1)	23775.3600	23775.3780	-0.0180 a
3(2, 2) - 2(2, 1)	23765.7400	23765.7122	0.0278 a
3(2, 1) - 2(2, 0)	23765.7400	23765.7122	0.0278 a
13(0, 13) - 12(0, 12)	102863.4090	102863.3920	0.0170
13(1, 13) - 12(1, 12)	102816.4410	102816.4496	-0.0086
13(1, 12) - 12(1, 11)	103021.2340	103021.2394	-0.0054
13(2, 12) - 12(2, 11)	102979.4650	102979.4483	0.0167
13(2, 11) - 12(2, 10)	102979.4650	102979.4484	0.0166
13(3, 10) - 12(3, 9)	102820.3910	102820.3950	-0.0040
14(0, 14) - 13(0, 13)	110774.9830	110774.9762	0.0068
14(1, 14) - 13(1, 13)	110724.4310	110724.4420	-0.0110
14(1, 13) - 13(1, 12)	110944.9540	110944.9691	-0.0151
14(2, 13) - 13(2, 12)	110899.9920	110899.9804	0.0116
14(2, 12) - 13(2, 11)	110899.9920	110899.9805	0.0115
14(3, 11) - 13(3, 10)	110728.6580	110728.6552	0.0028
18(0, 18) - 17(0, 17)	142418.9730	142418.9689	0.0041
18(1, 18) - 17(1, 17)	142354.1100	142354.1136	-0.0036
18(1, 17) - 17(1, 16)	142637.5600	142637.5519	0.0081
18(2, 17) - 17(2, 16)	142579.8110	142579.8135	-0.0025
18(2, 16) - 17(2, 15)	142579.8110	142579.8136	-0.0026
18(3, 15) - 17(3, 14)	142359.3060	142359.3126	-0.0066
19(0, 19) - 18(0, 18)	150329.2980	150329.3030	-0.0050
19(1, 19) - 18(1, 18)	150260.8840	150260.8804	0.0036
19(1, 18) - 18(1, 17)	150560.0440	150560.0357	0.0083
19(2, 18) - 18(2, 17)	150499.0990	150499.1215	-0.0225
19(2, 17) - 18(2, 16)	150499.0990	150499.1215	-0.0225
19(3, 16) - 18(3, 15)	150266.3080	150266.3017	0.0063
22(0, 22) - 21(0, 21)	174058.4490	174058.4614	-0.0124
22(1, 22) - 21(1, 21)	173979.3720	173979.3728	-0.0008
22(1, 21) - 21(1, 20)	174325.6200	174325.6498	-0.0298
22(2, 21) - 21(2, 20)	174255.2460	174255.2399	0.0061
22(2, 20) - 21(2, 19)	174255.2460	174255.2398	0.0062
23(0, 23) - 22(0, 22)	181967.5130	181967.5142	-0.0012
23(1, 23) - 22(1, 22)	181884.8940	181884.8833	0.0107
23(1, 22) - 22(1, 21)	182246.8850	182246.8568	0.0282
23(2, 22) - 22(2, 21)	182173.2910	182173.2932	-0.0022
23(2, 21) - 22(2, 20)	182173.2910	182173.2931	-0.0021
23(3, 20) - 22(3, 19)	181891.0810	181891.0804	0.0006

a Ref. (1)

Table 5

Observed and calculated rotational transitions in MHz of $\text{H}^{14}\text{N}^{12}\text{C}^{77}\text{Se}$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs.	calc.	obs-calc
2(0, 2) - 1(0, 1)	15874.1700	15874.1670	0.0030 a
2(1, 2) - 1(1, 1)	15866.9300	15866.8546	0.0754 a
2(1, 1) - 1(1, 0)	15898.5100	15898.5672	-0.0572 a
3(0, 3) - 2(0, 2)	23811.2400	23811.2112	0.0288 a
3(1, 3) - 2(1, 2)	23800.2800	23800.2434	0.0366 a
3(1, 2) - 2(1, 1)	23847.8300	23847.8116	0.0184 a
3(2, 2) - 2(2, 1)	23838.0400	23838.0340	0.0060 a
3(2, 1) - 2(2, 0)	23838.0400	23838.0340	0.0060 a
13(0, 13) - 12(0, 12)	103176.4870	103176.4657	0.0213
13(1, 13) - 12(1, 12)	103129.0420	103129.0457	-0.0037
13(1, 12) - 12(1, 11)	103335.0830	103335.0884	-0.0054
13(2, 12) - 12(2, 11)	103292.8250	103292.8136	0.0114
13(2, 11) - 12(2, 10)	103292.8250	103292.8136	0.0114
14(0, 14) - 13(0, 13)	111112.1280	111112.1266	0.0014
14(1, 14) - 13(1, 13)	111061.0580	111061.0783	-0.0203
14(1, 13) - 13(1, 12)	111282.9520	111282.9548	-0.0028
14(2, 13) - 13(2, 12)	111237.4450	111237.4453	-0.0003
14(2, 12) - 13(2, 11)	111237.4450	111237.4454	-0.0004
18(0, 18) - 17(0, 17)	142852.4140	142852.4123	0.0017
18(1, 18) - 17(1, 17)	142786.8990	142786.8973	0.0017
18(1, 17) - 17(1, 16)	143072.0590	143072.0716	-0.0126
18(2, 17) - 17(2, 16)	143013.6630	143013.6643	-0.0013
18(2, 16) - 17(2, 15)	143013.6630	143013.6644	-0.0014
19(0, 19) - 18(0, 18)	150786.8240	150786.8157	0.0083
19(1, 19) - 18(1, 18)	150717.6960	150717.6971	-0.0011
19(1, 18) - 18(1, 17)	151018.6830	151018.6853	-0.0023
23(0, 23) - 22(0, 22)	182521.2640	182521.2854	-0.0214
23(1, 23) - 22(1, 22)	182437.8270	182437.8141	0.0129
23(1, 22) - 22(1, 21)	182802.0250	182802.0082	0.0168
23(2, 22) - 22(2, 21)	182727.5860	182727.5913	-0.0053
23(2, 21) - 22(2, 20)	182727.5860	182727.5912	-0.0052

a Ref. (1)

Table 6

Observed and calculated rotational transitions in MHz of $\text{H}^{14}\text{N}^{12}\text{C}^{76}\text{Se}$ in the ground vibrational state

$J'(K'_a, K'_c) - J''(K''_a, K''_c)$	obs.	calc.	obs-calc
2(0, 2) - 1(0, 1)	15923.7500	15923.7376	0.0124 a
2(1, 2) - 1(1, 1)	15916.4100	15916.3480	0.0620 a
2(1, 1) - 1(1, 0)	15948.1900	15948.2583	-0.0683 a
3(0, 3) - 2(0, 2)	23885.5700	23885.5669	0.0031 a
3(1, 3) - 2(1, 2)	23874.5200	23874.4832	0.0368 a
3(1, 2) - 2(1, 1)	23922.3400	23922.3481	-0.0081 a
3(2, 2) - 2(2, 1)	23912.5200	23912.4586	0.0614 a
3(2, 1) - 2(2, 0)	23912.5200	23912.4586	0.0614 a
13(0, 13) - 12(0, 12)	103498.6360	103498.6448	-0.0088
13(1, 13) - 12(1, 12)	103450.7280	103450.7183	0.0097
13(1, 12) - 12(1, 11)	103658.0510	103658.0519	-0.0009
13(2, 12) - 12(2, 11)	103615.2850	103615.2842	0.0008
13(2, 11) - 12(2, 10)	103615.2850	103615.2842	0.0008
14(0, 14) - 13(0, 13)	111459.0920	111459.0835	0.0085
14(1, 14) - 13(1, 13)	111407.5000	111407.4890	0.0110
14(1, 13) - 13(1, 12)	111630.7640	111630.7567	0.0073
14(2, 13) - 13(2, 12)	111584.7040	111584.7148	-0.0108
14(2, 12) - 13(2, 11)	111584.7040	111584.7148	-0.0108
18(0, 18) - 17(0, 17)	143298.4700	143298.4676	0.0024
18(1, 18) - 17(1, 17)	143232.2580	143232.2456	0.0124
18(1, 17) - 17(1, 16)	143519.2090	143519.2147	-0.0057
18(2, 17) - 17(2, 16)	143460.0980	143460.1139	-0.0159
18(2, 16) - 17(2, 15)	143460.0980	143460.1140	-0.0160
19(0, 19) - 18(0, 18)	151257.6410	151257.6421	-0.0011
19(1, 19) - 18(1, 18)	151187.7260	151187.7757	-0.0497
19(1, 18) - 18(1, 17)	151490.6590	151490.6603	-0.0013
19(2, 18) - 18(2, 17)	151428.3360	151428.3054	0.0306
19(2, 17) - 18(2, 16)	151428.3360	151428.3055	0.0305
23(0, 23) - 22(0, 22)	183091.1780	183091.1793	-0.0013
23(1, 23) - 22(1, 22)	183006.8130	183006.7949	0.0181
23(1, 22) - 22(1, 21)	183373.2970	183373.2947	0.0023
23(2, 22) - 22(2, 21)	183297.9660	183297.9735	-0.0075
23(2, 21) - 22(2, 20)	183297.9660	183297.9734	-0.0074

a Ref. (1)

tion caused by the large rotational constant A , the unfavourable isotopic distribution of the HNCSe isotopomers and the hazards of extrapolating the spectrum of a quasilinear molecule.

3. Substitution Structure

The observed rotational constants B and C can be used together with published data [1] to refine the preliminary r_s -structure with support of the infrared data, which has been reported in our previous paper [2]. Landsberg explained the observed microwave spectrum of HNCSe [1] in terms of a linear molecular model. The preliminary r_s -structure [1] was consequently based on effective rotational constants, which correspond to $(B + C)/2$ in the case of the asymmetric top. These effective rotational constants differ significantly by 7 to 12 MHz from the rotational constants B obtained in this work on the basis of an asymmetric top molecular model. Since we know HNCSe is a quasilinear molecule which is nearer the bent limiting case, its rotational spectrum can be more adequately described by an asymmetric top model.

As the rotational constant A could not be determined from these spectra, only the coordinates of the nuclei along the a -axis were determined according to Kraitchman's equations [16, 17]. The molecular parameters used for the refinement of the r_s -structure are given in Table 9. The rotational constants B of $\text{H}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$ and $\text{H}^{14}\text{N}^{12}\text{C}^{78}\text{Se}$ have been determined in the present paper. The values of the remaining isotopomers were calculated by least squares fits of the transitions measured by Landsberg [1]. In the case of $\text{H}^{14}\text{N}^{13}\text{C}^{80}\text{Se}$ the quartic centrifugal distortion constants D_J and D_{JK} of the main isotopic species were used and held fixed during the fit, whereas in the case of $\text{D}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$ the molecular parameters were determined

Table 7a
Rotational and centrifugal distortion constants in the S-reduced Hamiltonian for the HNCSe isotopomers in the ground vibrational states^{a)}

	H ¹⁴ N ¹² C ⁸² Se	H ¹⁴ N ¹² C ⁸⁰ Se	H ¹⁴ N ¹² C ⁷⁸ Se	H ¹⁴ N ¹² C ⁷⁷ Se	H ¹⁴ N ¹² C ⁷⁶ Se
<i>A</i> /GHz	1700 ^{b)}	1700 ^{b)}	1700 ^{b)}	1700 ^{b)}	1700 ^{b)}
<i>B</i> /MHz	3918.7995(10)	3941.0395(5)	3964.3844(8)	3976.4752(7)	3988.9173(9)
<i>C</i> /MHz	3903.3977(10)	3925.4638(5)	3948.6243(8)	3960.6188(7)	3972.9620(9)
<i>D_J</i> /kHz	0.63214(53)	0.63946(19)	0.64652(46)	0.65035(41)	0.65377(53)
<i>D_{JK}</i> /kHz	−2483.30(33)	−2495.33(23)	−2508.19(38)	−2514.49(28)	−2520.74(36)
<i>d₁</i> /Hz	−5.00(53)	−4.97(17)	−5.24(42)	−5.18(41)	−4.85(53)
<i>d₂</i> /Hz	−2.18(19)	−2.23(9)	−2.28(18)	−2.31(22)	−2.34(25)
<i>H_{JK}</i> /Hz	4.41(25)	4.91(15)	4.78(35)	4.97(19)	4.74(25)
<i>H_{KJ}</i> /kHz	−383.792(58)	−385.612(59)	−387.785(90)	−388.354(54)	−389.198(70)
<i>L_{JK}</i> /Hz	0.76 ^{c)}	0.756(18)	0.730(37)	0.76 ^{c)}	0.76 ^{c)}
<i>L_{KJ}</i> /kHz	−9.78 ^{c)}	−9.7805(42)	−9.8586(65)	−9.78 ^{c)}	−9.78 ^{c)}
<i>σ</i> /kHz	18.0	14.0	16.2	15.2	19.8

^{a)} In brackets standard deviations in units of the last significant figures; − ^{b)} Assumed, held fixed during the least squares fit; − ^{c)} Value of the main isotopic species, held fixed during the fit.

Table 7b
Correlation matrix of the adjusted spectroscopic constants obtained for H¹⁴N¹²C⁸⁰Se ^{a)}

	<i>A</i> − <i>B</i> *	<i>B</i> *	<i>D_J</i>	<i>D_{JK}</i>	<i>d₁</i>	<i>d₂</i>	<i>H_{JK}</i>	<i>H_{KJ}</i>	<i>L_{JK}</i>	<i>L_{KJ}</i>
<i>A</i> − <i>B</i> *	1	0.92	0.69	0.66	0.43	0	0	0	0.52	0.26
<i>B</i> *		1	0.52	0.72	0.20	0	0	0	0.57	0.02
<i>D_J</i>			1	0.71	0.87	0.01	0	0	0.67	0.68
<i>D_{JK}</i>				1	0.34	0	0	0	0.93	0.04
<i>d₁</i>					1	0.01	0.01	0	0.37	0.95
<i>d₂</i>						1	0.94	0	0	0.01
<i>H_{JK}</i>							1	0	0	0.01
<i>H_{KJ}</i>								1	0	0
<i>L_{JK}</i>									1	0.07
<i>L_{KJ}</i>										1

^{a)} *B** = (*B* + *C*)/2.

Table 8
Rotational and centrifugal distortion constants in the S-reduced Hamiltonian for the main isotopomers of the HNCX molecules in the ground vibrational states^{a)}

	HNCO ^{b)}	HNCS ^{c)}	HNCSe ^{d)}
<i>A</i> /GHz	918.5044(154)	1361.53(81)	1700 ^{e)}
<i>B</i> /MHz	11071.00825(61)	5883.4628(3)	3941.0395(5)
<i>C</i> /MHz	10910.57553(61)	5845.6114(3)	3925.4638(5)
<i>D_J</i> /kHz	3.4863(29)	1.19419(41)	0.63946(19)
<i>D_{JK}</i> /kHz	931.70(65)	−1025.32(31)	−2495.33(23)
<i>D_K</i> /GHz	6.066(19)	57.52(32)	—
<i>d₁</i> /Hz	−72.995(83)	−13.7808(33)	−4.97(17)
<i>d₂</i> /Hz	−36.5(30)	−4.59(20)	−2.23(9)
<i>H_{JK}</i> /Hz	−2.49(16)	0.919(79)	4.91(15)
<i>H_{KJ}</i> /kHz	32.29(30)	−185.28(12)	−385.612(59)
<i>H_K</i> /MHz	287.6(41)	6038(52)	—
<i>L_{JK}</i> /Hz	—	—	0.756(18)
<i>L_{KJ}</i> /kHz	3.163(44)	−16.569(14)	−9.7805(42)
<i>L_K</i> /MHz	14.88(36)	363.2(36)	—
<i>S_{KJ}</i> /Hz	144.4(15)	−531.28(49)	—
<i>S_K</i> /MHz	0.493(15)	10.43(11)	—
<i>T_{KJ}</i> /Hz	2.494(48)	—	—
<i>T_K</i> /kHz	8.56(30)	111.3(13)	—
<i>U_K</i> /Hz	58.6(22)	—	—

^{a)} In brackets standard deviations in units of the last significant figures; − ^{b)} Ref. [14]; − ^{c)} Ref. [15]; − ^{d)} Present work; − ^{e)} Assumed, not adjusted.

Table 9
Rotational constants used for the refinement of the r_s -structure of isoselenocyanic acid, HNCSe

Isotopomer	This work		Landsberg ^{a)}	
	B/MHz	$I_0/\text{amu nm}^2$	$\frac{B+C}{2}/\text{MHz}$	$I/\text{amu nm}^2$
$\text{H}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$	3941.0395	1.2823419	3933.242	1.2848841
$\text{H}^{14}\text{N}^{12}\text{C}^{78}\text{Se}$	3964.3844	1.2747906	3956.495	1.2773326
$\text{H}^{14}\text{N}^{13}\text{C}^{80}\text{Se}$	3903.73 ^{b)}	1.2945977 ^{b)}	3896.277	1.2970741
$\text{D}^{14}\text{N}^{12}\text{C}^{80}\text{Se}$	3672.93 ^{b)}	1.3759478 ^{b)}	3661.358	1.3802966

^{a)} Ref. [1]; – ^{b)} See text.

in the non-rigid rotor model. The resulting coordinates calculated from the constants given in Table 9 are listed and compared with Landsberg's data in Table 10. As in Landsberg's study [1] the coordinate of the nitrogen nucleus was calculated from the first moment equation. Consequently the coordinates obtained differ only slightly from Landsberg's structural parameters for HNCSe.

Since the b -coordinates could not be determined, some assumptions must be made in order to complete an r_s -structure of this molecule. In analogy with the r_s -structures of the lighter pseudohalogen hydrazides, in which the heavy atoms are not bound in a linear, but in a slightly trans bent planar configuration [14, 18–20], an NCSe bond angle of 175° has been assumed by linear extrapolation of the NCX angles (see Fig. 4). The NH internuclear distance was assumed to be 99 pm, which satisfies Bernstein's rule [21] correlating NH distances with NH

Table 10
 a -coordinates of the nuclei in HNCSe in the principal axis system in pm obtained from the data given in Table 9

Nucleus	Present work	Ref. [1]
H	306.4	309.4
N	230.2 ^{a)}	230.3 ^{a)}
C	111.0	110.8
Se	–60.9	–60.9

^{a)} Obtained from the first moment equation.

stretching vibrational wavenumbers. With the knowledge of the a -coordinates of the nuclei H and N and assuming the NH internuclear distance the bond angle could be obtained. The resulting HNC bond angle fits well in the series of the lighter homologs. The r_s -structure of HNCSe obtained is illustrated and compared with the r_s -structures of HN_3 [18], HNCO [14] and HNCS [19]. For the last two molecules a recalculation of the r_s -structure [20] led to a similar result using a least squares fit to the rotational constants of all known isotopomers. Comparing the structures of these molecules it is obvious that the arrangement of the heavy atoms approaches the linear configuration with the heavier substituents. In the same sequence the NH internuclear distances shrink slightly, whereas the HNC bond angles are distinctly enlarged.

4. Conclusions

Rotational and centrifugal distortion constants were determined for five isotopomers of HNCSe in natural abundance. Using the information obtained from the rotational and vibrational spectra the quasilinearity parameter γ can be estimated by dividing the rotational constant A by the frequency of the quasilinear fundamental vibration according to Eqs. (1) and (2). The fundamental ν_5 of HNCSe, from the preceding paper [2], can be observed at 419 cm^{-1} or 12.6 THz in the matrix, whereas the value of A is estimated from the structure discussed above, leading to $\gamma_0 = 0.46$. In the group of four-atomic pseudohalogen hydrazides hydrazoic acid, HN_3 , whose quasilinearity parameter γ_0 is 0.93, is among the typically bent molecules. HNCO , HNCS and HNCSe show up as successively more quasilinear molecules, with γ_0 dropping successively from 0.84 for HNCO to 0.61 for HNCS to about 0.46 for HNCSe . Indeed the most quasilinear molecule in this series is isoselenocyanic acid, HNCSe , whose quasilinear behaviour is also exhibited in the large centrifugal distortion observed in the present study. Unfortunately the low yield of the preparation used and the

Fig. 4

r_s -structure of four-atomic pseudohalogen hydrazides (internuclear distances given in pm). The NH internuclear distance and the NCSe bond angle are assumed for HNCSe, thus leading to a partial r_s -structure. The values given in parentheses are quoted by the authors listed in parentheses: Ref. [18] for HN_3 , Refs. [14] and [20] for HNCO , Refs. [19] and [20] for HNCS , this paper and Ref. [1] for HNCSe

instability of HNCSe made it so far impossible to obtain more extensive data on this enticingly quasilinear molecule.

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References

- [1] B. M. Landsberg, *Chem. Phys. Lett.* **60**, 265 (1979).
- [2] J. Vogt and M. Winnewisser, *Ber. Bunsenges. Phys. Chem.* **88**, 439 (1984).
- [3] K. Yamada and M. Winnewisser, *Z. Naturforsch.* **31a**, 139 (1976).
- [4] P. R. Bunker and D. J. Howe, *J. Mol. Spectrosc.* **83**, 288 (1980).
- [5] K. Yamada and M. Winnewisser, *J. Mol. Spectrosc.* **68**, 307 (1977).
- [6] K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. L. Gerry, *J. Mol. Spectrosc.* **64**, 401 (1977).
- [7] J. Bendtsen and M. Winnewisser, *Chem. Phys. Lett.* **33**, 141 (1975).
- [8] W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, *Can. J. Phys.* **53**, 1869 (1975).
- [9] L. B. Szalanski, M. C. L. Gerry, G. Winnewisser, K. Yamada, and M. Winnewisser, *Can. J. Phys.* **56**, 1297 (1978).
- [10] M. Winnewisser, *Z. Angew. Phys.* **30**, 359 (1971).
- [11] M. Winnewisser and B. P. Winnewisser, *Z. Naturforsch.* **29a**, 633 (1974).
- [12] D. A. Helms, M. Winnewisser, and G. Winnewisser, *J. Phys. Chem.* **84**, 1758 (1980).
- [13] J. K. G. Watson, Aspects of Quartic and Sextic Centrifugal Effects on Rotational Energy Levels, in: J. R. Durig, *Vibrational Spectra and Structure*, Elsevier, Amsterdam.
- [14] K. Yamada, *J. Mol. Spectrosc.* **79**, 323 (1980).
- [15] K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. L. Gerry, *J. Mol. Spectrosc.* **78**, 189 (1979).
- [16] J. Kraitchman, *Am. J. Phys.* **21**, 17 (1953).
- [17] W. Gordy and R. L. Cook, *Microwave Molecular Spectra*, in: W. West, *Chemical Application of Spectroscopy*, Part II, Wiley-Interscience, New York 1970.
- [18] B. P. Winnewisser, *J. Mol. Spectrosc.* **82**, 220 (1980).
- [19] K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. L. Gerry, *J. Mol. Spectrosc.* **79**, 295 (1980).
- [20] L. Nemes, *Kem. Közl.* **54**, 378 (1980).
- [21] H. J. Bernstein, *Spectrochim. Acta* **18**, 161 (1962).

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Diffusion Coefficients and Thermal Diffusion Factors of Several Binary Systems of Carbon Monoxide and Oxygen with Noble Gases

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Diffusion / Gases / Statistical Mechanics / Thermal Diffusion / Transport Properties

Diffusion coefficients and thermal diffusion factors are reported for several binary systems of carbon monoxide and oxygen with noble gases. Using approximate spherical potential functions, most of which have been reported in the literature, the experimental results are compared with the predictions of the Chapman-Enskog theory.

Introduction

In previous publications [1–8] we have reported diffusion coefficients and thermal diffusion factors for many binary gaseous systems. The purpose of this paper is to report similar data for several binary mixtures of carbon monoxide and oxygen with noble gases, and to compare some of the data with corresponding theoretical values predicted by means of the Chapman-Enskog theory [9, 10] and the potential functions for like and unlike interactions which have been reported in the literature.

Experimental

Binary diffusion coefficients, $\mathcal{D}_{12}$, were measured in a stainless steel two-bulb cell which has been described in detail previously [11, 12]. Thermal diffusion factors, α_T , were obtained from the steady state mole fractions, x_1 , of the heavy component in the two bulbs of a cell maintained with a temperature difference of approximately 50 K between the bulbs. The α_T values were calculated from the relations

$$\alpha_T = \ln q / \ln (T'/T) \quad (1a)$$

$$q = [x_1/(1-x_1)]/[x'_1/(1-x'_1)] \quad (1b)$$

where T is the absolute temperature, q is the separation, and a prime on a variable indicates a value corresponding to the higher temperature. The results for the analysis of a typical experiment are shown in Table 1.

Table 1^{a)}
Typical calibration of the thermal conductivity cell and the analysis of the two bulbs of the thermal diffusion cell
Exp. 172 B: He–CO
 $T^1 = 326.12 \text{ K}$; $T = 275.40 \text{ K}$

Bottle No.	Bridge reading (mV)	x_1 (Calibration)	x_1 (Least-square)	δx_1 ($\cdot 10^4$)
1	–3.810	0.2200 ₅	0.2200 ₅	0.0
2	–2.509	0.2100 ₈	0.2101 ₀	–0.2
3	–1.196	0.2000 ₁	0.1999 ₆	+0.5
4	0.089	0.1899 ₂	0.1899 ₆	–0.4
5	1.339	0.1801 ₆	0.1801 ₅	+0.1
Top bulb	1.036		0.1825 ₄	
Bottom bulb	–0.643		0.1956 ₇	

^{a)} The values of x_1 (calibration) were least-squared to a parabola in the corresponding values of the bridge reading. The top and bottom bulb concentrations were obtained by interpolation.