The CHNO Isomers

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The recent isolation of isofulminic acid has opened the door for a comparative study of all the four possible CHNO isomers: isocyanic acid, cyanic acid, fulminic acid, and isofulminic acid. Their infrared spectra have been measured in an argon matrix at 13 K and are compared with the results of ab initio calculations.

Die CHNO-Isomeren

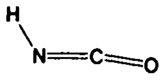
Die kürzlich gelungene Isolierung von Isoknallsäure hat das Tor für eine vergleichende Studie über alle vier möglichen CHNO Isomere (Isocyansäure, Cyansäure, Knallsäure und Isoknallsäure) geöffnet. Ihre Infrarot-Spektren, aufgenommen in einer Argon-Matrix bei 13 K, werden mit den Ergebnissen von ab-initio-Rechnungen verglichen.

The family of compounds with the empirical formula CHNO and their salts have played an especially important role in the development of chemistry. Although these compounds have been the subject of chemical research since the sixteenth century, our knowledge of them is still incomplete.

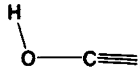
The earliest known representatives of this family are the salts of fulminic acid. The preparation of the gold salt (gold fulminate) was described by alchemists such as S. Schwaertzer (active from 1585 in the court of the Saxon elector) and his contemporary, the Benedictine monk Basilius Valentinus. The mercury salt (mercury fulminate) was already known to Cornelius Drebbel (1572–1634) and to Johann Kunckel von Löwenstern (1630–1703). The interest in these salts of fulminic acid was not purely accidental: we certainly owe the wealth of literature left by the alchemists to the simple preparation and the usefulness as explosives of these salts.

Almost two centuries later, in 1823–1825, the silver salts of fulminic acid and isocyanic acid were at the center of one of the most important discoveries of modern chemistry. On determining the empirical formula of silver fulminate, Liebig and Gay-Lussac[1] observed that a year earlier Wöhler had found exactly the same empirical formula for silver cyanate (called "Cyansilber" by Wöhler). After some less than pleasant arguments and a careful reexamination of the work of both Liebig and Wöhler, later great friends, had to recognize that in spite of different properties the two substances actually had the same empirical formula. A year later, the term "isomerism" was coined for this concept[2]. It is not surprising that August Kekulé, a student of Liebig, also studied mercury fulminate[3], but it is little known that this work was the first in which the quadrivalence of carbon was recognized[2].

Among the acids, isocyanic acid was the first obtained. In an 1830 publication Liebig and Wöhler reported the preparation of isocyanic acid[4], which was later improved by Adolf Baeyer[5]. By 1890, the preparation of pure isocyanic acid gas had become routine, and the synthesis described at that time by Gattermann still has general applicaton today[6]. Astonishingly, isocyanuric acid, the trimer of isocyanic acid needed for this synthesis, was already at that time a commercial compound.

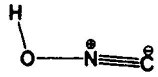


Isocyanic acid



Cyanic acid

Fulminic acid



Isofulminic acid

With respect to its isolation, fulminic acid proved to be somewhat stubborn. Although Liebig and Gay-Lussac had already studied the action of hydrochloric acid on silver fulminate[1], Wieland and Hess[7] were the first who succeeded in showing that fulminic acid can exist both in ether solution and in the gas phase. The isolation of the pure substance was first achieved much later by Beck and collaborators[8].

The structure of isocyanic acid was also clear much earlier than that of fulminic acid. In 1933, Birckenbach suggested that isocyanic acid has the carbimide structure[9]. Stimulated by this suggestion, Goubeau[10] studied the Raman spectrum of isocyanic acid and confirmed that it exists exclusively in the ketimine form. This was later confirmed by the measurement of the IR spectrum in the gas phase[11,12]. Unfortunately, because of some doubtful chemical proofs, the idea still lingers today in many textbooks that, at least in solution, isocyanic acid is in equilibrium with its tautomer, cyanic acid. But still more regrettable are the misunderstandings that appear in *Chemical Abstracts* where work that deals with isocyanic acid can be found under "Cyanic acid [420-05-3]" as well as under "Isocyanic acid [75-13-8]".

The structure of fulminic acid proved much more difficult to determine. In the beginning, polymeric structures were considered, but finally Nef[13], in 1894, recognized that fulminic acid consists of only an atom each of C, N, O, and H. The carbon monoxide oxime proposed by him was generally accepted, although the chemical arguments on which it was based were anything but unambiguous.

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However, one must consider the extremely complicated chemistry of fulminic acid, which was finally clarified by Grundmann and coworkers[14] in 1973. The isolation of fulminic acid and the recording of its IR spectrum by Beck et al.[8,15,16] shows that it has the formonitrile oxide rather than the carbon monoxide oxime structure. This was confirmed by the microwave[17–19] and far infrared[20] spectra. It is interesting to note that Pauling had already calculated in 1926 that the formonitrile oxide structure should be more stable than the carbon monoxide oxime structure[21], but this prediction remained unnoticed.

The list of important advances in chemistry with which fulminic and isocyanic acid are connected does not end with the concepts of isomerism and structural theory. Most recently, fulminic acid is central in the development of the theory of quasi-linear molecules. These molecules, for which the Born-Oppenheimer separation of rotation and vibration no longer holds, are still today the subject of much research, which has been reviewed by B. P. Winnewisser[22].

For a long time, isocyanic acid and fulminic acid remained the only representatives of the CHNO family. Finally, in 1964, Jacox and Milligan could show that, on irradiating matrix-isolated isocyanic acid at short wavelengths ($\lambda \approx 224$ nm), a photoequilibrium with the isomeric cyanic acid occurs[23]. Later, Bondybey et al.[24] showed that irradiation of matrix-isolated fulminic acid also produced cyanic acid. In spite of many efforts, these two remain the only methods of producing cyanic acid, and neither allows the production of high concentrations in a matrix nor a synthesis in the gas phase.

The interest in the CHNO isomers was reawakened in 1977 by the theoretical work of Poppinger, Radom, and Pople[25] who calculated the energy hypersurface by ab initio methods. According to their results, isofulminic acid should be an isolable compound as well as isocyanic acid, cyanic acid, and fulminic acid. Other theoretical work that appeared at about the same time supported these conclusions[26,27] (Figure 1).

The reaction of experimentalists followed soon. Four years after the appearance of the theoretical work, Wentrup et al.[28] succeeded in isolating the methyl and phenyl esters of isofulminic acid. The isolation of the parent isofulminic acid in an argon matrix at 13 K has recently been accomplished[29] in our laboratory.

Energies and Structures

Only very little is known experimentally about the energies of the CHNO isomers. The energy of formation is known only for isocyanic acid (-24 ± 3 kcal/mol)[30,31]. Hence, one must fall back on theoretical predictions. In the theoretical work of Rauk and Alewood[27] and of McLean, Loew, and Berkowitz[26] the geometries of only some of the isomers were optimized. Poppinger, Radom, and Pople[25] give many data for the optimized structures of all isomers but only with relatively modest basis sets. We have, therefore, calculated the structure, energies, and infrared spectra of isocyanic acid, cyanic acid, fulminic acid, and isofulminic acid at the MP2/6-31G** level. As can be seen in Figure 2, the relative energy of the four isomers depends on the calculation. The large energy oscillations for fulminic acid and isofulminic acid are striking.

Of the two CHNO isomers already known in the gas phase, the structure of isocyanic acid is the better known. Because the three heavy atoms almost lie on the *a* axis, the Kraitchmen equation provides no reliable value for their distances from this axis. The problem can be overcome, however[32], and the structure obtained from the measured moments of inertia is in good agreement with our MP2/6-31G** theoretical structure (Figure 3). The angles, where the greatest discrepancy might have been expected, are especially well reproduced by the calculation.

However, problems appear if one makes the analogous comparison for fulminic acid. The problem arises because with the word structure different things are meant depending on the context. If one calculates an ab initio structure, one

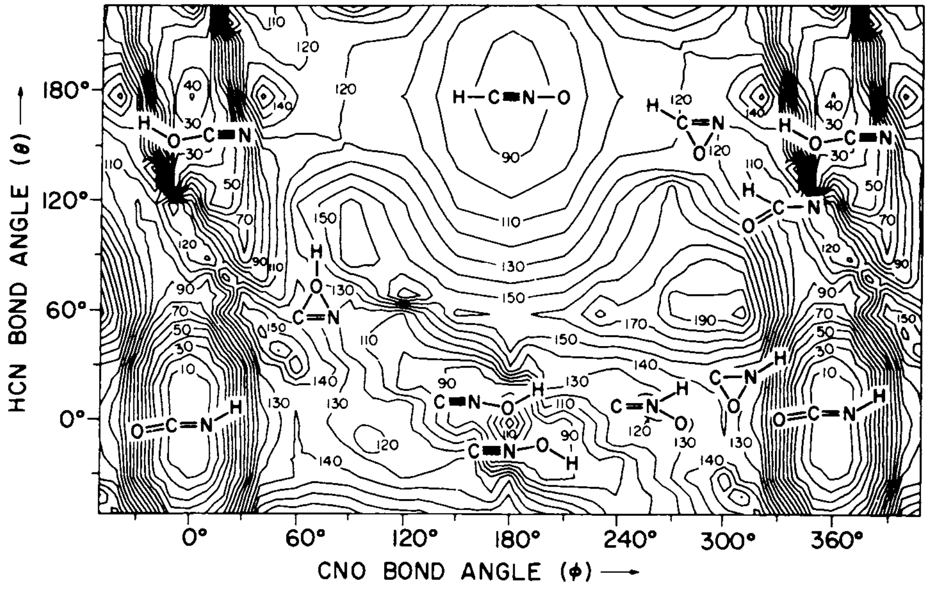

Figure 1. The SCF/4-31G theoretical energy surface of CHNO from Poppinger, Radom, and Pople[25]; contours [kcal/mol] (reprinted with permission from ref.[25]; © 1977 American Chemical Society)

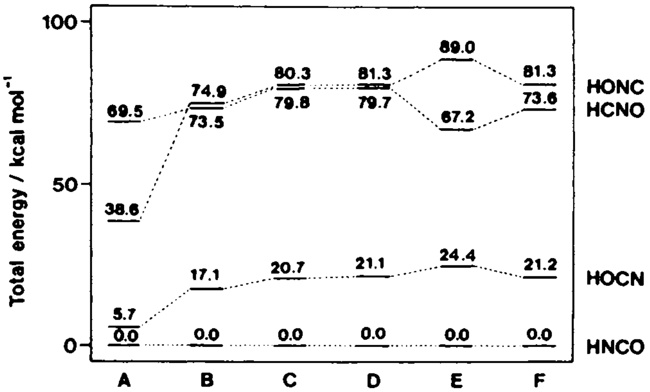

Figure 2. Energies [kcal/mol] of the CHNO isomers relative to isocyanic acid; **A** = SCF/STO-3G optimized energy; **B** = SCF/4-31G energy at the geometry of **A**; **C** = SCF/4-31G optimized energy; **D** = SCF/6-31G* energy at geometry of **C**; **E** = MP2/6-31G** optimized energy; **F** = CCD (coupled cluster, double excitation) optimized energy; the MP2/6-31G** and the CCD results are from the present work, the others are from ref.[25]; the quality of the calculations increases from left to right

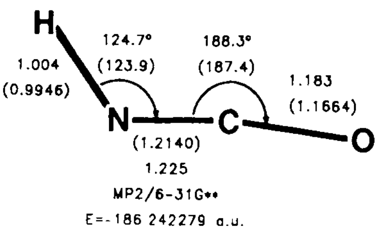

Figure 3. The theoretical MP2/6-31G** structure of isocyanic acid; values in parentheses are from the r_s structure of Yamada[32]; values for internuclear distances [Å], angles [°]

gets an atomic arrangement that corresponds to a minimum in the energy hypersurface (equilibrium or r_e structure). In contrast, structures which are calculated from the measured moments of inertia (r_0, r_s, or r_m structures) are only approaches to the equilibrium structure. This is due to the fact that it is very difficult to account for the atomic motions, which are present even in the ground state vibrational level (see for instance ref.[33]). For molecules that have only small amplitudes of vibration, this difference is of little significance, but this does not carry over to molecules with large vibrational amplitudes for which r_e and r_0 structures may differ markedly. Quasilinear molecues, such as fulminic acid, are molecules with large vibrational amplitudes (see ref.[22] for a review). In the case of fulminic acid, an experimentally determined structure could only be defined in combination with a determination of the HCN bending potential function (see ref.[47]).

In a very complete work Farnell, Nobes, and Radom[34] have compared their theoretical MP3/6-31G** structure for fulminic acid with experiment (see ref.[47]). Because a comparison of our MP2/6-31G** structure with experiment would be repetition of this work, it is more meaningful to compare the two calculated structures (Figure 4). The MP3 equilibrium structure is linear while the MP2 structure is bent (the linear MP2 structure is only 0.64 kcal/mole higher in energy than the bent one and has one imaginary vibrational frequency). An important point is that both ab initio bending potentials define a broad, nearly flat potential well characteristic of a quasilinear molecule. For a consistent comparison of all four isomers on the basis of our calculated spectra, the MP2 potential and a bent model were used in predicting the HCNO spectrum, even though the experimental spectrum in the gas phase is more easily labeled as that of a linear molecule.

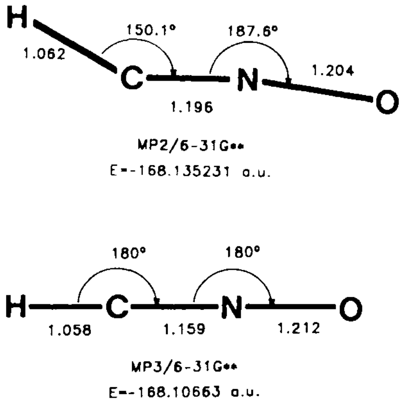

Figure 4. The calculated structures of fulminic acid; the MP3 data are from Farnell, Nobes, and Radom[34]

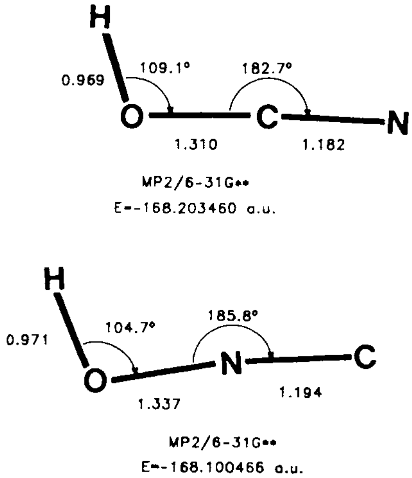

Figure 5. The MP2/6-31G** energies and structures of cyanic acid and isofulminic acid

Since there are experimental data for neither the structure nor energy of cyanic acid and isofulminic acid, the calculated energies and structures are given in Figure 5 without comment.

Photochemistry

The photochemistry of isocyanic acid in the gas phase was investigated by Okabe[30] and is well described (for a review see ref.[31]). The vacuum UV photochemistry of matrix-isolated isocyanic acid was studied by Milligan and Jacox[35]. They found that irradiation of matrix-isolated isocyanic acid below 224 nm led to photoequilibrium between isocyanic acid and cyanic acid.

Until now, the photochemistry of fulminic acid has been studied only in rare-gas matrices. Irradiation of matrix-isolated fulminic acid in the vacuum UV leads to splitting into H and the CNO radical, which then isomerizes very easily to the NCO radical, as Bondybey et al. found by analyzing the UV spectrum[36]. However, in the IR spectrum cyanic acid and isocyanic acid are the only products observed[24].

From the UV spectrum of fulminic acid in the gas phase[37] one can conclude that the 254-nm line of a low-pressure mercury lamp should be especially suited for the photolysis. Fulminic acid, isolated in an argon matrix, photolyzed with 254-nm light gave cyanic acid and isocyanic acid as the only identifiable products. In addition, a weak band at 3270.4 cm^{-1} can be seen. This band shifts on ^{13}C and ^{15}N substitution to 3252.0 and 3268.5 cm^{-1}, respectively, and can be assigned to no known molecule. The hypothesis that this might be the C–H stretching vibration of triplet formylnitrene is refuted by ab initio calculations since this stretching vibration should give an especially weak band.

Isofulminic acid is relatively inert photochemically. On irradiation with 254-nm light it slowly isomerizes to isocyanic acid[29].

IR Spectra

Isocyanic acid and fulminic acid and their deuterated isotopomers are the only ones of the four CHNO isomers which had been studied in the gas phase. While the spectra of isocyanic acid and fulminic acid are well understood, there remain some unclear points in the spectra of the deuterated isotopomers. The ν_4 fundamental of deuteriofulminic acid has not yet been found either in the gas phase or in a rare-gas matrix. Further, the assignments of the ν_4 and ν_5 fundamental vibrations of deuterioisocyanic acid by Ashby and Werner[38] are probably incorrect. The earlier assignment by Carlotti et al.[39] of the rotational structure of the ν_1 vibration of isocyanic acid has also recently been recognized as in error[22,40] (Table 1).

Table 1. Fundamental wavenumbers [cm^{-1}] of isocyanic acid, fulminic acid and deuterated isotopomers in the gas phase

Vibration	HNCO	DNCO	HCNO	DCNO
1	3538.24469[40]	2637.198[42]	3336.1[55]	2620.7267[58]
2	2268.8921[52,53]	2235[38]	2195.8[55]	2070.9170[59]
3	1327[11,12]	1310[38]	1253.4[55]	1254[16]
4	776.623[44]	460*[38]	537.250[20,56]	**
5	577.347[44]	766.8*[38]	224.1071[20,57]	162.7[20]
6	656.29***[44,54]	602.9[38]		

* Assignment probably incorrect. – ** Never observed. – *** Calculated from data of ref.[44,54]; never directly observed.

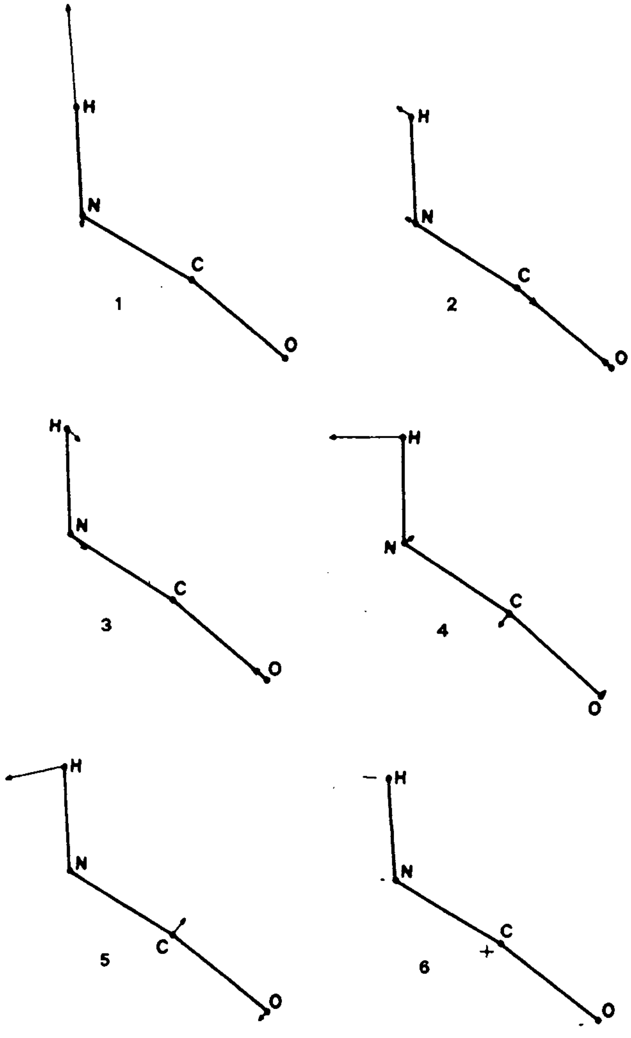

Figure 6. The normal coordinates of isocyanic acid

Table 2. Rotationless transitions in the infrared spectra of isocyanic acid and its isotopomers in an argon matrix [cm^{-1}]

Vibration		Symmetry	HNCO		DNCO		HN^{13}CO		H^{15}NCO	
1	ν_{NH}	A'	3516.8 3505.7	*0.13*[a] *0.13*	2606.9	*0.23*	3514.9 3507.3 3502.0	*0.14* *0.11* *0.03*	3502.6	*0.20*
2	ν^{as}_{NCO}	A'	2259.0	*1.00*	2231.0	*1.00*	2199.0	*1.00*	2250.8	*1.00*
3	ν^{s}_{NCO}	A'								
4	δ_{HNC}	A'	769.8	*0.16*	578.6	*0.06*	758.8	*0.17*	764.4	*0.23*
5	δ_{NCO}	A'	573.7	*0.15*	475.4	*0.05*	566.3	*0.14*	573.0	*0.24*
6	δ_{NCO}	A''								
4 + 5		A'	1315.0	*0.007*	1036.6	*0.004*	1307.7	*0.006*	1303.6	*0.009*

[a] *Italic* figures are relative integrated intensities.

Table 3. MP2/6-31G** theoretical infrared transitions of isocyanic acid and its isotopomers [cm^{-1}]

Vibration		Symmetry	HNCO		DNCO		HN^{13}CO		H^{15}NCO	
1	ν_{NH}	A′	3796	*0.32*[a]	2805	*0.40*	3796	*0.33*	3787	*0.31*
2	ν^{as}_{NCO}	A′	2377	*1.00*	2348	*1.00*	2310	*1.00*	2386	*1.00*
3	ν^{s}_{NCO}	A′	1316	*0.0004*	1297	*0.002*	1316	*0.0004*	1294	*0.0006*
4	δ_{HNC}	A′	792	*0.50*	703	*0.17*	784	*0.54*	786	*0.50*
5	δ_{NCO}	A′	564	*0.16*	470	*0.21*	553	*0.15*	563	*0.16*
6	δ_{NCO}	A″	617	*0.002*	601	*0.02*	601	*0.001*	616	*0.0002*

[a] *Italic* figures are relative calculated intensities.

The IR spectra of isocyanic acid and fulminic acid in the gas phase are very complex because of the quasilinearity of these molecules, and a detailed discussion is not possible here. We refer instead to the review by B. P. Winnewisser[22]. Neither cyanic acid nor isofulminic acid have yet been observed in the gas phase. We have been able to produce all four CHNO isomers, and in addition several isotopomers, in argon matrices and to record their IR spectra under identical conditions (argon matrix at 13 K, host: guest ≈ 5000: 1, resolution 0.5 cm^{-1}). We have also been able to interpret these spectra satisfactorily with the aid of ab initio theoretical spectra.

Isocyanic Acid

Isocyanic acid is the most stable isomer with the composition CHNO. Although isocyanic acid can be easily isolated or generated in situ by pyrolysis of its trimer isocyanuric acid, its direct condensation with an excess of argon is not satisfactory if very good matrix-isolated samples are needed. Isocyanic acid forms very strong hydrogen bonds, and the formation of dimers can scarcely be avoided. These dimers have bands in the same region as the ν_1 fundamental of isocyanic acid monomer and impede the analysis of this band which is already complex in itself. To get around this problem, isocyanic acid and its ^{13}C and ^{15}N isotopomers were generated in the matrix by the photolysis of fulminic acid which can be easily isolated. This trick cannot be used for deuterioisocyanic acid because its ν_1 fundamental overlaps the ν_1 fundamental of deuteriofulminic acid. Deuterioisocyanic acid was generated in situ by the flash vacuum pyrolysis of deuterated isocyanuric acid (about 75% deuterated after a single recrystallization from methan-[D]ol).

Table 4. Perpendicular and parallel components of the transition moments of the fundamental vibrations of isocyanic acid

Vibration		Symmetry	% Perpendicular	% Parallel
1	ν_{NH}	A′	30	70
2	ν^{as}_{NCO}	A′	0	100
3	ν^{s}_{NCO}	A′	8	92
4	δ_{HNC}	A′	17	83
5	δ_{NCO}	A′	0	100
6	δ_{NCO}	A″	100	0

Isocyanic acid belongs to the point group C_s. There are five vibrational fundamentals of A' symmetry and one of A''. The corresponding normal coordinates are shown in Figure 6. Only four of these six fundamentals can be found. (In addition, a rovibrational band of a fifth fundamental was measured.) Their wavenumbers and intensities are collected in Table 2. For comparison, the wavenumbers and intensities from the MP2/6-31G** calculation are given in Table 3.

A very important point in the interprepation of the IR spectrum is the fact that an isocyanic acid molecule isolated in an argon matrix can rotate almost freely around its a axis. This was already recognized by Cugley and Pullin[41] who measured the far-infrared spectrum of isocyanic acid and deuterioisocyanic acid in an argon matrix. The value they found for the A rotational constant agrees well with the value from the gas phase.

How distinct the rotational structure is depends on the character of the individual bands. For pure perpendicular bands, that is bands where the transition dipole is perpendicular to the a axis, the selection rule $\Delta K_a = \pm 1$ holds. For parallel bands on the other hand $\Delta K_a = 0$ where K_a is the quantum number for rotation around the a axis. The perpendicular and parallel components of the transition dipoles are collected in Table 4.

The ν_1 Band. The ν_1 band of isocyanic acid (the N−H stretch) is a hybrid band, and transitions with $\Delta K_a = 0$ are allowed as well as with $\Delta K_a = \pm 1$. In view of the relatively large A constant for isocyanic acid (about 30 cm^{-1}) and the very low temperature, only transitions from the ground state with $K_a = 0$ should be observable. Then only two bands would be expected: a strong Q-absorption feature for the transition $0 \leftarrow 0$ (from $K_a = 0$ in the ground state to $K_a = 0$ in the excited state) and a weaker R feature for the transition $1 \leftarrow 0$. Actually, more than two bands are observed, and their number depends also on the isotopic substitution pattern as is shown in Figure 7.

There are two reasons why several bands are observed. In the first place, the $1 \leftarrow 0$ transition for all isotopomers is split into a triplet. This is caused by interaction with the argon cage. The potential term in the rotation Hamiltonian no longer vanishes as for free rotation, but is a function of the rotation angle Θ. The matrix perturbation on the shape of the potential $V(\Theta)$ is, however, weak, and it causes only a lifting of the degeneracy in the levels with $K_a > 0$.

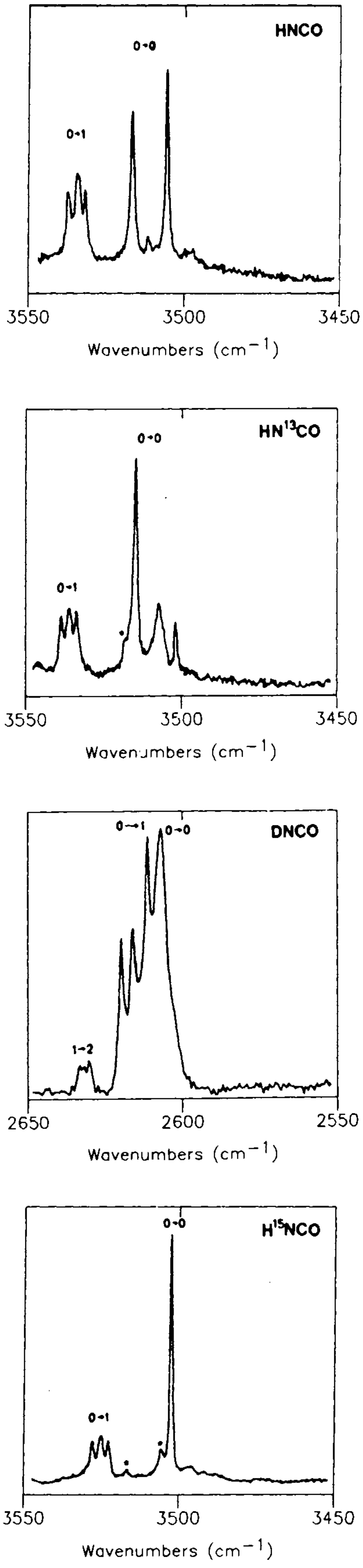

Figure 7. The ν_1 fundamental of several isotopomers of isocyanic acid; bands marked with * belong to the unlabeled isocyanic acid

$$\hat{H} = -\frac{\hbar^2}{2I_a}\frac{d^2}{d\Theta^2} + V$$

$V = 0$ for free rotation
$V = V(\Theta)$ for rotation in the argon matrix

On the other hand, there is also in isocyanic acid and [^{13}C]isocyanic acid a perturbation of the Q feature ($0 \leftarrow 0$ transition) by Fermi resonance. Fermi type resonances that perturb the energy levels with $K_a = 2$ and 4 are also observed in the gas phase[40] (Figure 8), and it is possible that the same overtone causes the perturbation in the argon matrix. With the data from the gas phase it was not possible to identify this overtone. In this respect the matrix data are more helpful since one can be certain that the two states that are in Fermi resonance both must have $K_a = 0$. The perturbing band in isocyanic acid is very likely the combination $\nu_2 + \nu_4 + \nu_5$. Because the relative intensities of the two bands in the Fermi doublet are known, one can calculate the position of the unperturbed ν_1 fundamental of isocyanic acid in argon (3511.3 cm^{-1}) and with it also the effective A constant for the ν_1 excited state. The value found (22.9 cm^{-1}) is in exceptional agreement with that (22.76 cm^{-1}) found by Yamada in the gas phase[40].

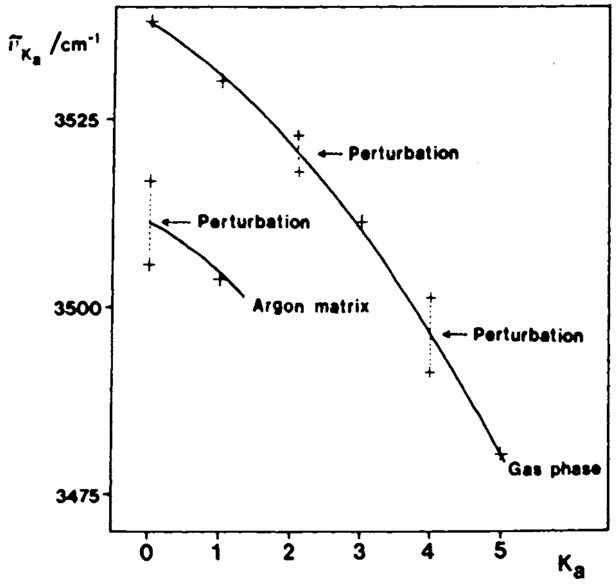

Figure 8. Plot of the location of the subband origins $\tilde{\nu}_{K_a} = E'_{K_a} - E''_{K_a}$ of the parallel component of the ν_1 band of isocyanic acid in an argon matrix and in the gas phase against the rotational quantum number K_a; the $K_a = 1$ point for the matrix was obtained from a perpendicular transition; gas phase data from Yamada[40]

In the case of [^{13}C]isocyanic acid, there is a threefold Fermi resonance between ν_1 and perhaps $\nu_2 + \nu_4 + \nu_5$ and $\nu_2 + \nu_3$. On the other hand the ν_1 bands of [^{15}N]isocyanic acid and deuterioisocyanic acid are not perturbed in the argon matrix by Fermi resonance.

Because of the smaller A constant in the ground vibrational state of deuterioisocyanic acid, even at 13 K, a non-negligible fraction of the molecules are in the rotational level with $K_a = 1$; and the transition $2 \leftarrow 1$ can also be observed (at about 2632 cm^{-1}). The measured value for the effective A rotational constant in the ν_1 excited state of deuterioisocyanic acid is only 9.6 cm^{-1}, much smaller than the value of 14.24 cm^{-1} found by Steiner et al.[42] This discrepancy is probably due to the fact that in the gas phase the ν_1 band is perturbed by the overtone $2\nu_3$[42]. This perturbation is absent in the argon matrix.

For [^{13}C]- and [^{15}N]isocyanic acid, the measured effective rotational constants in an argon matrix are 22 cm^{-1} and 22.5 cm^{-1}, respectively.

The ν_2 Band. The ν_2 band (asymmetric NCO stretch) is almost purely parallel, and as such shows only a single absorption (Q feature). This is the strongest band for all isotopomers of isocyanic acid.

The ν_3 Band. The ν_3 band of isocyanic acid (symmetric NCO stretch) is very weak in the gas phase and lies at about 1327 cm^{-1}[11]. Bondybey et al.[24] assigned a band observed at 1320.4 cm^{-1} in a neon matrix to the ν_3 fundamental. They could not find the corresponding band for deuterioisocyanic acid and argued that deuterioisocyanic acid is "more symmetric" than isocyanic acid since masses to the left and to the right of the carbon atom are almost equal. This argument is contradicted by ab initio calculations, which show that in the case of deuterioisocyanic acid and [^{15}N]isocyanic acid, where this "symmetry" is greatest, the ν_3 band is the most intense (relative intensities: HNCO = 1.00, DNCO = 4.74, HN^{13}CO = 1.05, H^{15}NCO = 1.42 according to MP2/6-31G** calculations). In an argon matrix, very weak bands of isocyanic acid and of the ^{13}C and ^{15}N isotopomers were also found in the same region. However, the isotopic shifts are not consistent with the assignment of this band to the ν_3 fundamental. The ^{13}C shift for the ν_3 fundamental should be almost zero (the calculated value is 0.1 cm^{-1}), but the observed value is 7.3 cm^{-1} for this band, which must therefore be assigned to the combination $\nu_4 + \nu_5$. This assignment also holds for deuterioisocyanic acid. The IR spectrum of deuterioisocyanic acid in an argon matrix shows no absorption in the ν_3 region but has a weak band at 1036.6 cm^{-1} where the $\nu_4 + \nu_5$ combination band would be expected. The actual ν_3 vibration in an argon matrix is much too weak to be observed in the IR spectrum. However, this band should be the most intense in the Raman spectrum of isocyanic acid.

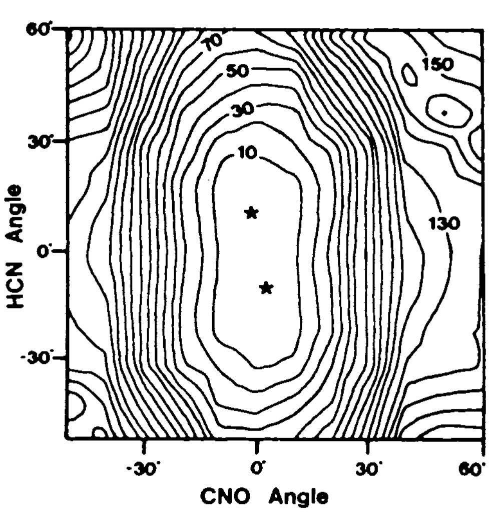

Figure 9. Section of the 4-31G energy hypersurface of CHNO in the region of isocyanic acid (from ref.[25]); contours [kcal/mol]; the two minima are marked with *

The ν_4 and ν_5 Bands. Although the ν_4 and ν_5 fundamentals of isocyanic acid would normally be described as HNC and NCO bends, this description is misleading. As Figure 6 clearly shows, both vibrations have a large contribution from the hydrogen motion. Fusina and Mills[43] have already called attention to this problem and described ν_4 as an "in-phase" and ν_5 as an "out-of-phase" combination of the two bending coordinates. This statement has several important consequences. It is readily seen (Figure 9) that the calculated energy hypersurface of Poppinger, Radom, and Pople[25] shows a large flat region describing the deformation of the HNC angle, a certain indication of quasilinearity. Since this deformation contributes to ν_4 as well as to ν_5, both vibrations are expected to be quasilinear and very anharmonic. It is, therefore, understandable why the combination band $\nu_4 + \nu_5$ is the only one observable in the argon matrix.

A second important consequence is that both fundamentals should show a large deuterium isotope shift. This is supported by the ab initio calculations, which predict a shift of about 90 cm^{-1} for both bands. The assertion by Ashby and Werner[38] that only one of the fundamentals is shifted casts doubt on their assignments. Bondybey et al.[24] who later obtained the IR spectrum of deuterioisocyanic acid in argon and neon matrices looked for ν_4 and ν_5 in the region of the gas phase values of Ashby and Werner and found the wrong bands. The band they found at 721.4 cm^{-1} certainly

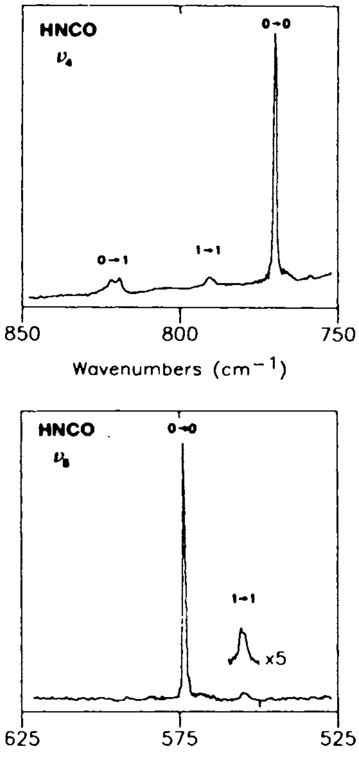

Figure 10. The rotational structure of the ν_4 and ν_5 fundamentals of isocyanic acid in an argon matrix

belongs to hydrogen cyanide. It is interesting that already in 1964 Milligan and Jacox[35] had found the correct ν_4 and ν_5 of deuterioisocyanic acid, but their work remained unnoticed (they were cited neither by Ashby and Werner nor by Bondybey et al.).

The fundamentals ν_4 and ν_5 show rotational structure in an argon matrix (Figure 10). ν_4 is a hybrid band, and in addition to the $0 \leftarrow 0$ transition the $1 \leftarrow 1$ (at 790.7 cm^{-1}; 797.876 cm^{-1} in the gas phase) and $1 \leftarrow 0$ (a doublet at 821.6 and 819.1 cm^{-1}; 827.96 cm^{-1} in the gas phase) transition for isocyanic acid were observed. On the other hand, ν_5 is a parallel band and besides the $0 \leftarrow 0$ only the $1 \leftarrow 1$ transition (at 554.5 cm^{-1}; 556.474 cm^{-1} in the gas phase) was observed for isocyanic acid (the gas phase data are from ref.[44]).

The ν_6-Band. The only band of isocyanic acid with A'' symmetry, ν_6, is a pure perpendicular band, and the intensity of the $0 \leftarrow 0$ transition should be zero. In fact the ab initio calculated intensity of ν_6 is almost zero, although larger than that calculated for ν_3. However, in the argon matrix the $1 \leftarrow 0$ transition should be observable. It is seen as a weak (intensity relative to ν_2: 0.024) and somewhat broadened band at 697 cm^{-1} (668 cm^{-1} for [^{13}C]isocyanic acid and 695 cm^{-1} for [^{15}N]isocyanic acid). The same transition was found in the gas phase at 699.73 cm^{-1}[44]. Bondybey et al.[24] report having observed the ν_6 fundamental of isocyanic acid at 668.4 cm^{-1} in a neon matrix. What they saw, however, was not a band of isocyanic acid but the incompletely compensated *Q*-absorption feature of the deformation fundamental of CO_2 in the air. This incomplete compensation can occur because of the circumstances of the measurement. With an FT-IR apparatus, reference and sample are measured at different times, and it is sometimes difficult to guarantee that the CO_2 concentration in the sample chamber remains the same for both measurements.

Isocyanic acid, the most stable CHNO isomer, is unique since it can rotate almost freely in an argon matrix. Although all fundamentals are shifted somewhat to lower frequency in comparison with the gas phase (between 27 cm^{-1} for ν_1 and only a few cm^{-1} for bending vibrations), the *A* rotational constant is almost unaltered. The principal effect of the argon matrix appears to be the removal of the degeneracy of rotational levels with $K_a > 0$.

Cyanic Acid

Cyanic acid is thermodynamically the second most stable of the CHNO isomers, but because of its kinetic instability it has only been studied under matrix conditions.

Cyanic acid belongs to the C_s point group and has six fundamental vibrations, five of A' symmetry and one of A''. The normal coordinates are shown in Figure 11. Examination of these normal coordinates and of the calculated energy hypersurface of Poppinger et al.[25] (Figure 12) shows that no quasilinearity is expected.

This is confirmed by the good agreement between the fundamental wavenumbers measured in an argon matrix and those from the ab initio calculation. The isotope shifts are also well reproduced, and there remains no doubt that these bands actually belong to cyanic acid. Experimental and calculated wavenumbers and intensities are collected in Tables 5 and 6.

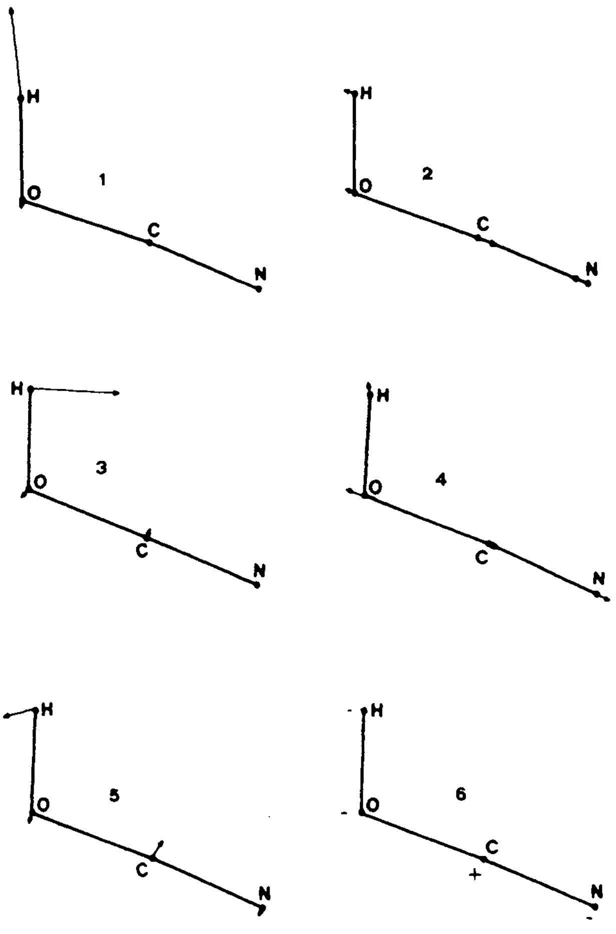

Figure 11. The normal coordinates of cyanic acid

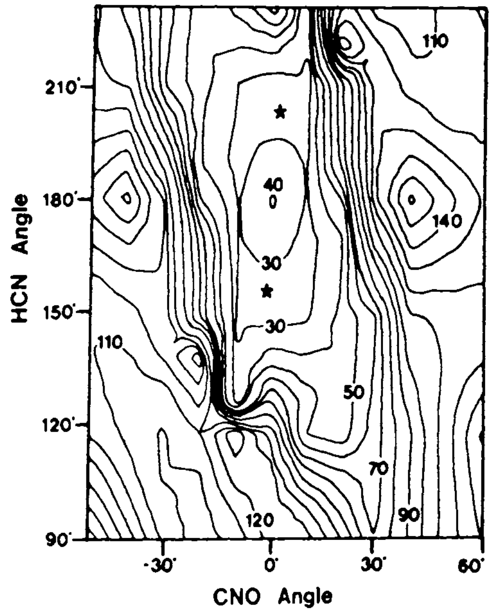

Figure 12. Section of the 4-31 G energy hypersurface of CHNO in the region of cyanic acid (from ref.[25]); contours [kcal/mol]; the two minima are marked with *

Table 5. Infrared transitions of cyanic acid and its isotopomers in an argon matrix [cm^{-1}]

Vibration	Symmetry	HOCN		DOCN		$HO^{13}CN$		$HOC^{15}N$	
1 ν_{OH}	A'	3569.6	*0.84*[a]	2635.0	*1.00*	3569.2	*0.87*	3569.3	*1.00*
2 ν_{CN}	A'	2286.3	*1.00*	2284.6	*0.97*	2232.5	*0.92*	2261.9	*0.97*
3 δ_{COH}	A'	1227.9	*0.92*	1077.8	*0.67*	1224.5	*1.00*	1227.0	*0.96*
4 ν_{CO}	A'	1081.3	*0.3*	949.4	*0.39*	1074.2	*0.5*	1069	*0.4*
5 δ_{OCN}	A'								
6 δ_{OCN}	A''								

[a] *Italic* figures are relative integrated intensities.

Table 6. MP2/6-31G** theoretical infrared transitions of cyanic acid and its isotopomers [cm^{-1}]

Vibration	Symmetry	HOCN		DOCN		$HO^{13}CN$		$HOC^{15}N$	
1 ν_{OH}	A'	3855	*1.00*[a]	2807	*1.00*	3855	*1.00*	3855	*1.00*
2 ν_{CN}	A'	2276	*0.43*	2273	*0.80*	2217	*0.39*	2254	*0.43*
3 δ_{COH}	A'	1253	*0.73*	1080	*0.77*	1250	*0.73*	1253	*0.75*
4 ν_{CO}	A'	1083	*0.42*	959	*0.52*	1080	*0.42*	1069	*0.39*
5 δ_{OCN}	A'	429	*0.11*	408	*0.20*	418	*0.10*	427	*0.11*
6 δ_{OCN}	A''	470	*0.03*	469	*0.08*	457	*0.02*	467	*0.02*

[a] *Italic* figures are relative calculated intensities.

Table 7. Perpendicular and parallel components of the transition moments of the fundamental vibrations of cyanic acid

Vibration	Symmetry	% Perpendicular	% Parallel
1 ν_{OH}	A'	59	41
2 ν_{CN}	A'	0	100
3 δ_{COH}	A'	1	99
4 ν_{CO}	A'	0	100
5 δ_{OCN}	A'	9	91
6 δ_{OCN}	A''	100	0

Although the molecular sizes and geometries of cyanic acid and isocyanic acid are not very different, cyanic acid shows no indication of rotation in the argon matrix. The calculation of the perpendicular and parallel components of all fundamentals (Table 7) shows that, if cyanic acid could rotate in the argon matrix, the ν_1 fundamental should show a marked rotational structure similar to that of isocyanic acid.

The ab initio calculated A constant of cyanic acid is 22.0 cm^{-1}, but the effective A constant for the ν_1 vibration should be smaller. That is, the $1 \leftarrow 0$ transition would be expected at a wavenumber about 20 cm^{-1} higher than the rotationless ν_1 transition. No bands were found for cyanic acid in this region, and it must be assumed that cyanic acid is not free to rotate in an argon matrix.

This is quite puzzling since hydrogen azide (HN_3), whose molecular structure[22] is almost identical to that of cyanic acid, does show – as we have determined – a clear rotational structure for the ν_1 band when isolated in an argon matrix ($0 \leftarrow 0$: 3316.8 cm^{-1}; $1 \leftarrow 0$: 3336 cm^{-1}).

Fulminic Acid

The analysis of the IR spectrum of fulminic acid, isolated in an argon matrix at 10 K, presents several difficult problems. For normal molecules, the energy difference between rotational levels (ΔE_R) is much smaller than that between vibrational levels (ΔE_V). In the case $\Delta E_R \approx \kappa^2 \Delta E_V$, where κ = (electron mass/proton mass)$^{1/4}$, it is possible to separate the Hamiltonian into rotational and vibrational parts[45]. For fulminic acid in the gas phase, the quasilinearity of fulminic acid makes this separation invalid. The HCN bending fundamental lies at only 224 cm^{-1} [20]. Therefore, the HCN bending vibration and the rotation around the a axis must be considered together (for a complete discussion see ref.[22,46]). The combination of these two motions (vibration and rotation) gives two rovibrational states that in the linear molecule normally would be called ν_5 and $2\nu_5$. (Note that in Table 1 the spectrum in the gas phase is labeled with the mode designations of a linear molecule, whereas in Tables 8–10 the labeling of a bent model is followed.)

In matrices, the IR spectrum of the bending modes of fulminic acid appears to change sharply. B. P. Winnewisser et al.[20] have studied the IR spectrum in HCN and n-hexane matrices at 80 K and found no indication for an absorption below 500 cm^{-1}. However, Bondybey et al.[24] found bands in the spectrum of matrix-isolated fulminic acid at 243 cm^{-1} (argon matrix) and 239 cm^{-1} (neon matrix). The intensities of these bands were not reported, and the spectrum is only shown to 400 cm^{-1}. In our work, we have measured the spectrum of fulminic acid, isolated in an argon matrix at 10 K, with a resolution of 0.5 cm^{-1} and also found a band at 243.6 cm^{-1}. However, this band does not belong to fulminic acid. It is present in the spectra of all isotopically substituted species and apparently shows no isotope shift. In our case, this feature was definitely an instrumental artifact. We find only three bands below 600 cm^{-1} for fulminic acid: a doublet at about 538 cm^{-1} that clearly belongs to the CNO bending vibration and a broader band at 566.6 cm^{-1} that we assign to the HCN bend (see Figure 13 and Table 8).

Table 8. Infrared transitions of fulminic acid and its isotopomers in an argon matrix [cm^{-1}]

Vibration		Symmetry	HCNO		DCNO		H^{13}CNO		HC^{15}NO	
1	ν_{CH}	A′	3317.2	*0.61*[a]	2612.7	*1.00*	3300.8	*0.53*	3314.5	*0.56*
2	ν^{as}_{CNO}	A′	2192.7	*1.00*	2063.2	*0.48*	2170.9	*1.00*	2149.5	*1.00*
3	ν^{s}_{CNO}	A′	1244.1	*0.34*	1218.5	*0.34*	1228.1	*0.32*	1241.0	*0.45*
4	δ_{HCN}	A′	566.6	*0.37*	418.7	*0.17*	560.4	*0.35*	564.8	*0.65*
5	δ_{CNO}	A′	536.9	*0.05*			535.8	*0.06*	526.4	*0.09*
6	δ_{CNO}	A″	538.2	*0.04*			537.1	*0.04*	527.5	*0.07*
2 + 3		A′	3415.9	*0.14*	3262.6	*0.07*	3378.5	*0.17*	3373.7	*0.22*
3 + 3		A′	2480.2	*0.06*	2428.4	*0.02*	2449.1	*0.07*	2473.0	*0.09*

[a] *Italic* figures are relative integrated intensities.

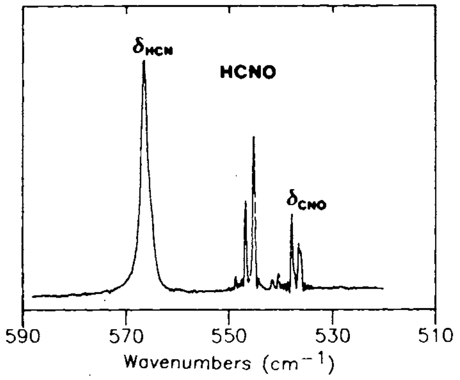

Figure 13. Absorption bands of fulminic acid in an argon matrix below 600 cm^{-1}; bands not marked belong to benzonitrile

The lack of a band in the IR spectrum of matrix-isolated fulminic acid (Table 8) that occurs in the gas phase at 224 cm^{-1} is not very surprising. First of all, even in the gas phase the band at 224 cm^{-1} is much weaker than its overtone at 540 cm^{-1}. A possible explanation of the matrix results is that through interaction with the matrix the energy hypersurface for HCN bending becomes very perturbed. The effect of this perturbation can be most easily understood with the aid of the correlation diagram from ref.[22], which is reproduced in Figure 14. The compression of the fulminic acid molecule by the matrix forces the two energy minima further apart and raises the barrier between them. That is, fulminic acid is shifted to the right in the correlation diagram when it is isolated in a matrix and thus behaves more as a bent molecule. As can be seen in the correlation diagram the ν_5^1 band (superscript gives the vibrational angular momentum, P, which correlates with K_a), which occurs at 224 cm^{-1} in the gas phase, becomes a rotation of the bent molecule and drops to very low wavenumber, while the $2\nu_5^0$ band, which occurs at 542 cm^{-1} in the gas phase[20,22], becomes a rotation of the bent molecule while the $2\nu_5^0$ band, which occurs at 537 cm^{-1} in the gas phase, becomes a bending vibration of the bent molecule without changing its energy substantially. This is the band that one finds in the IR spectrum at 566.6 cm^{-1} for fulminic acid isolated in a matrix.

This explanation has a weak point since it is very improbable that the matrix can have so large an effect on the energy hypersurface. For example, the energy surface of isocyanic acid, which is also a quasilinear molecule, is scarcely perturbed. If, however, the matrix does have a large effect, it would then be expected that the IR spectrum of fulminic acid would be very sensitive to the type of matrix; but this is not the case (see Table 10).

There is a different possibility that would explain the observed spectrum. As already mentioned, isocyanic acid in an argon matrix can rotate nearly freely around its *a* axis, but neither cyanic acid nor isofulminic acid can do this, although their structures are similar. One can ask what the effect on the IR spectrum of fulminic acid would be if rotation around the *a* axis were not possible. In this case, the HCN bending vibration would be decoupled from the rotation and the spectrum would appear as though the Born-Oppenheimer separation were valid. It would then be expected that the HCN bending vibration of matrix-isolated fulminic acid would appear at about the same wavenumber as the $2\nu_5^0$ level of fulminic acid in the gas phase. The reason for this can be explained in a few words. Although ν_5^1 and $2\nu_5^0$ are rovibrational bands, ν_5^1 has primarily rotational character. This becomes especially significant if one calculates the A rotational constant for the "semirigid bender" structure of fulminic acid[22]. The calculated value of 207.2 cm^{-1} lies only 16.9 cm^{-1} lower than the ν_5^1 band in the gas phase; for a pure rotational motion, these values would be equal. Correspondingly, the $2\nu_5^0$ band has mainly vibrational character.

This also would explain why in the spectrum from the ab initio calculation (Table 9), in which the bent MP2 structure was used and the Born-Oppenheimer separation was assumed, the HCN bending wavenumber is calculated to be nearly equal to that of $2\nu_5^0$. What is calculated is the wavenumber of the vibrational mode in the bent model, which should be at the same wavenumber as $2\nu_5^0$. Actually, this band which is assigned to the HCN bend of matrix-isolated fulminic acid is some 30 cm^{-1} higher than $2\nu_5^0$ in the gas phase.

Now let us ask what would be the effect on the spectrum of fulminic acid if rotation in the matrix were possible. As in HNCO, the stretching modes ν_2 und ν_3 are pure parallel bands, and would reveal no structure due to rotation. Since HCNO is so nearly linear, the transition moment of ν_1 must also be almost entirely parallel to the figure axis, so that again no structure due to rotation is expected. The band

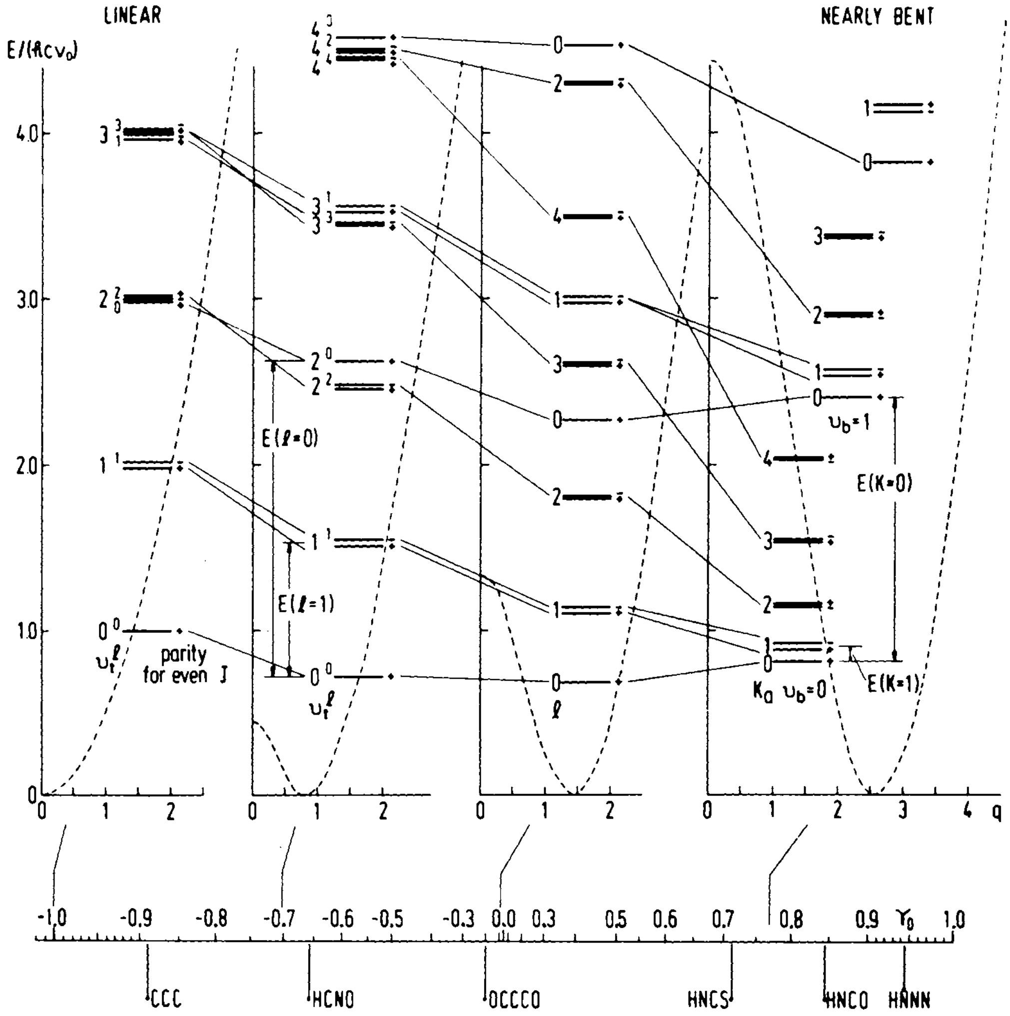

Figure 14. Correlation between bending-potential functions and energy levels of linear and bent molecules; the coordinate q is the dimensionless bending coordinate; each potential curve shows a section through an isotropic, two-dimensional potential function; the scale below shows the position of some molecules in the scale of the quasilinearity parameter γ_0; for the definition of γ_0 see ref.[22]

Table 9. MP2/6-31G** theoretical infrared transitions of fulminic acid and its isotopomers [cm^{-1}]

Vibration		Symmetry	HCNO		DCNO		H^{13}CNO		HC^{15}NO	
1	ν_{CH}	A'	3537	*0.43*[a]	2704	*0.94*	3521	*0.41*	3536	*0.44*
2	ν^{as}_{CNO}	A'	2282	*1.00*	2197	*1.00*	2266	*1.00*	2232	*1.00*
3	ν^{s}_{CNO}	A'	1332	*0.08*	1301	*0.10*	1309	*0.07*	1331	*0.09*
4	δ_{HCN}	A'	582	*0.20*	418	*0.28*	582	*0.19*	579	*0.23*
5	δ_{CNO}	A'	496	*0.15*	519	*0.003*	491	*0.15*	488	*0.14*
6	δ_{CNO}	A''	581	*0.004*	546	*0.002*	579	*0.004*	569	*0.005*

[a] *Italic* figures are relative calculated intensities.

assigned to the HCN bend at 566.6 cm^{-1} is, in either the bent or linear description, a $\Delta K_a = 0$ transition. Among the observed transition, only the CNO bending mode (ν_4 in the linear notation) at 536.9/538.2 cm^{-1} is a perpendicular band.

If there is little change from the gas phase spectrum, the average of the calculated A' and A'' δ(CNO) modes in the bent model should correspond to the degenerate δ(CNO) mode in the quasilinear model and in the observed spectrum. This expectation is satisfactorily fulfilled. The small splitting (1.3 cm^{-1}) of the absorption assigned to the CNO bending mode could be a matrix site effect, but it could also be a hindered rotation effect, as observed in HNCO, since the upper state, in the linear molecule, correlates with a $K_a = 1$ level. The lack of a doublet in the nitrogen matrix – the data from a neon matrix were recorded at lower resolution (Table 10) – is consistent with this interpretation.

Table 10. Vibrational wavenumbers [cm^{-1}] of fulminic acid in various matrices

Vibration		Symmetry	Argon, 13 K[a]	Nitrogen, 13 K[b]	Neon, 4 K[c]
1	ν_{CH}	A'	3317.2	3311	3338
2	ν^{as}_{CNO}	A'	2192.7	2200	2200
3	ν^{s}_{CNO}	A'	1244.1	1232	1250
4	δ_{HON}	A'	566.6	582	560
5	δ_{CNO}	A'	536.9	528	539
6	δ_{CNO}	A''	538.2		
3 + 3		A'	2480.2	2458	2492
2 + 3		A'	3419.9	3410	3430

[a] Resolution: 0.5 cm^{-1}. — [b] Resolution: 1 cm^{-1}. — [c] From ref.[24]; resolution: 2 cm^{-1}.

Whether or not HCNO can rotate in the matrix cannot be decided unambiguously on the basis of the available data, since a band corresponding to the linear ν_5 fundamental could not be detected.

Isofulminic Acid

According to MP2/6-31G** calculations, isofulminic acid is a planar, bent molecule with C_s symmetry. Five A' and one A'' vibrational fundamentals are expected with the normal coordinates shown in Figure 15.

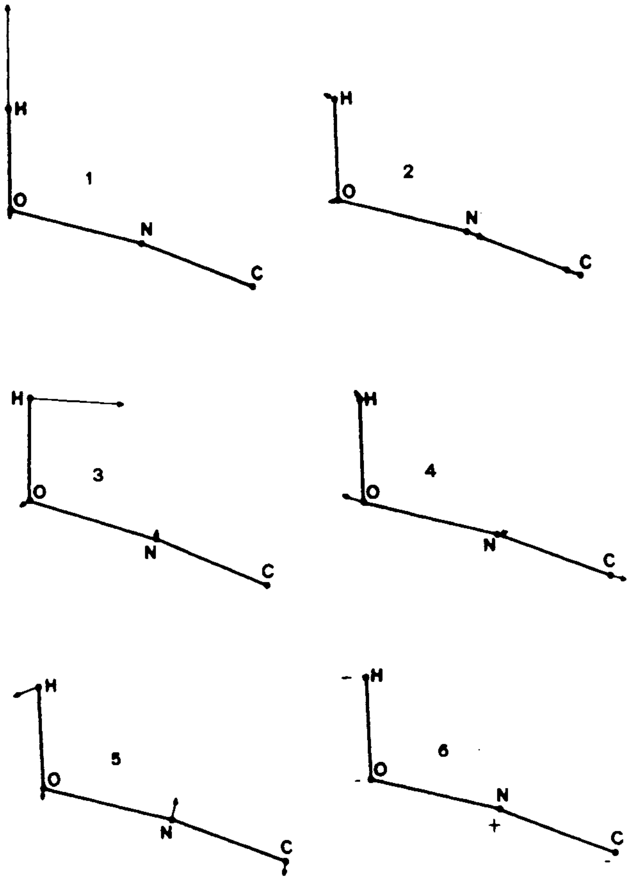

Figure 15. The normal coordinates of isofulminic acid

The calculated energy hypersurface of Poppinger, Radom, and Pople[25] in the neighborhood of the isofulminic acid minimum shows that the CNO moiety must be very flexible (see Figure 16). This view is also supported by the MP2/6-31G** calculation, which predicts a still flatter potential surface for the CNO in-plane deformation. This energy surface is approximately given by $E/h \cdot c$ [cm^{-1}] $= 4996.9 \cdot (\Theta - \Theta_{min})^2 + 524.3 \cdot (\Theta - \Theta_{min})^4$ where Θ is the CNO angle in radians and $\Theta_{min} = 3.042$ rad is the equilibrium CNO angle. The amplitude of the CNO deformation would be then about ± 10° in the ground state and ± 20° in the first vibrational excited state ($\nu_5 = 1$). The effects of this very anharmonic energy surface for the heavy atoms on the IR spectrum of isofulminic acid are difficult to predict.

In the argon-matrix spectrum both in-plane bending vibrations show relatively strong overtones (Table 11) as is consistent with a very anharmonic bending potential. Further, the MP2/6-31G** theoretical IR spectrum, calculated in the harmonic approximation, shows a poorer agreement with the experimental spectrum than was seen for the other isomers (Table 12). Nevertheless, the spectral pattern is correctly reproduced.

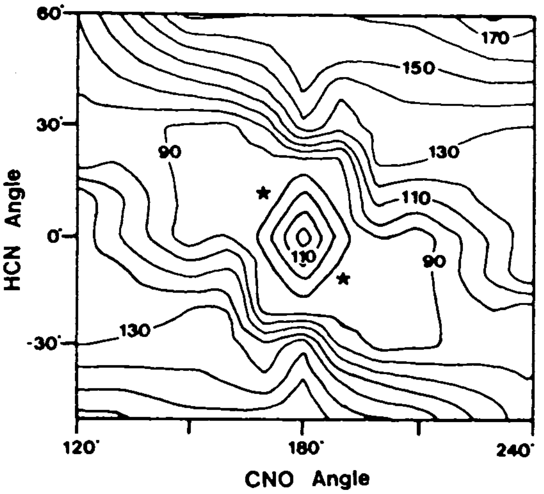

Figure 16. Section of the 4-31G energy hypersurface in the region of isofulminic acid (from ref.[25]); contours [kcal/mol]; the two minima are marked with *

Table 11. Infrared transitions of isofulminic acid and deuterioisofulminic acid in an argon matrix [cm^{-1}]

Vibration		Symmetry	HONC		DONC	
1	ν_{OH}	A'	3443.7	*1.00*[a]	2545.2	*1.00*
2	ν_{NC}	A'	2190.1	*0.15*	2190.3	*0.13*
3	δ_{NOH}	A'	1232.4	*0.30*	902.6	*0.22*
4	ν_{NO}	A'	628.4	*0.03*	623.1	*0.04*
5	δ_{ONC}	A'	361.2	*0.03*	357.3	*0.03*
6	δ_{ONC}	A''	379.3	*0.05*	362.1	*0.05*
3 + 3		A'	2443.7	*0.04*	1793.5	*0.03*
5 + 5 or 6 + 6		A'	679.0	*0.01*		

[a] *Italic* figures are relative integrated intensities.

Table 12. MP2/6-31G** theoretical infrared transitions of isofulminic acid and deuterioisofulminic acid [cm^{-1}]

Vibration	Symmetry	HONC		DONC	
1 ν_{OH}	A'	3803	*1.00*[a]	2770	*1.00*
2 ν_{NC}	A'	2139	*0.03*	2135	*0.03*
3 δ_{NOH}	A'	1416	*0.69*	1059	*0.88*
4 ν_{NO}	A'	1001	*0.37*	998	*0.52*
5 δ_{ONC}	A'	274	*0.06*	267	*0.10*
6 δ_{ONC}	A''	319	*0.02*	315	*0.002*

[a] *Italic* figures are relative calculated intensities.

Table 13. Perpendicular and parallel components of the transition moments of the fundamental vibrations of isofulminic acid

Vibration	Symmetry	% Perpendicular	% Parallel
1 ν_{OH}	A'	60	40
2 ν_{NC}	A'	7	93
3 δ_{NOH}	A'	0	100
4 ν_{NO}	A'	0	100
5 δ_{ONC}	A'	11	89
6 δ_{ONC}	A''	100	0

Like cyanic acid and fulminic acid, isofulminic acid cannot rotate around its *a* axis in an argon matrix. Were it able to rotate, the data in Table 13 imply that the ν_1 band would have to show a clear rotational structure.

The ν_1 Band. The ν_1 band of isofulminic acid (O–H stretch) occurs at a very low energy. Although substituted formoximes have O–H stretching frequencies around 3600 cm^{-1}, this band in isofulminic acid is some 150 cm^{-1} lower. Such a low wavenumber for the O–H stretching vibration has been found only in H–O–O · (3414 cm^{-1} in an argon matrix[48]) and indicates a very weak O–H bond.

The ν_2 Band. The ν_2 band (N–C stretch) occurs in isofulminic acid about 100 cm^{-1} lower than in cyanic acid. This difference is of the same order of magnitude as has been seen for the corresponding esters (about 80 cm^{-1})[28,49]. A more interesting point is the effect of methyl substitution. The ν_{CN} band of methyl cyanate lies about 50 cm^{-1} lower than the corresponding band of unsubstituted cyanic acid. The same is seen in methyl isofulminate whose ν_{NC} stretch is some 30 cm^{-1} below that of isofulminic acid.

The ν_4 Band. The largest discrepancy between theory and experiment is in the ν_4 band (N–O stretch) of isofulminic acid. According to the ab initio calculations the N–O stretch of isofulminic acid should be at 1001 cm^{-1}. This appears to be a reasonable result since computed wavenumbers are typically 10% too high and such vibrations normally occur at around 900 cm^{-1}. For example, in formoxime it lies at 888 cm^{-1}[50] and in hydroxylamine at 895 cm^{-1}[51]. Actually, in the IR spectrum of the photoproduct of dibromoformoxime, the precursor of isofulminic acid[29], one finds a band near 940 cm^{-1}, but no absorption is found in this region after photolysis of deuteriodibromoformoxime although the N–O stretch in deuterioisofulminic acid should be stronger than that in isofulminic acid. It is doubtful that this band belongs to isofulminic acid at all. We assign the N–O stretch to a band at 628.4 cm^{-1} (623.1 cm^{-1} for deuterioisofulminic acid), which shows the expected deuterium isotope shift. This is, of course, an unusually low energy for an N–O stretch, and this band could also be an overtone of ν_5 or ν_6. The analysis of the IR spectrum of other isotopomers is absolutely necessary for the resolution of this problem.

The Bending Vibrations. For the reasons already given, the bending vibrations should be very anharmonic. It is also not surprising that the agreement between calculated and observed bands is only fair. Nevertheless, the large difference between the wavenumbers of the CNO bending vibrations in fulminic acid and isofulminic acid is correctly predicted.

Although it appears to be no easy task, efforts to measure the IR spectrum of isofulminic acid in the gas phase are in progress.

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Experimental

Infrared Spectra: The reported infrared spectra were taken on a Bruker IFS 85 FT infrared spectrometer with a resolution of 0.5 cm^{-1} covering the range of 4000–300 cm^{-1}. For the matrix experiments the double-stage compressor "Displex Closed-Cycle Refrigeration System CS 202" from Air Products was used.

CAS Registry Numbers

HNCO: 75-13-8 / NCOH: 420-05-3 / $C^- \equiv N^+ - OH$: 506-85-4 / $HC \equiv N = O$: 51060-05-0 / $C^- \equiv N^+ - OD$: 20411-64-7 / $DO - CN$: 65627-65-8 / $HO - {}^{13}C \equiv N$: 118832-13-6 / $HO - C \equiv {}^{15}N$: 118832-14-7 / ${}^{13}C^- \equiv N^+ - OH$: 118832-15-8 / $C^- \equiv {}^{15}N^+ - OH$: 118832-16-9 / $D - C \equiv N = O$: 118832-17-0

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