

PREDICTION OF HIGHER INVERSION ENERGY LEVELS FOR ISOCYANAMIDE H₂NNC

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The lowest inversion energies of the pyramidal molecule isocyanamide H₂NNC have been predicted using the semirigid inverter model. The calculation was based on an *ab initio* inversion potential function which we have refined by fitting it to the experimental data available for H₂NNC. It is hoped that the predicted energies will make it possible to assign further transitions of H₂NNC.

Ab initio calculations (see ref.¹ and references therein) have shown that isocyanamide H₂NNC (Fig. 1) is pyramidal at equilibrium with a barrier to planarity around 2 000 cm⁻¹, and thus it is possible to observe the effects of the inversion with standard spectroscopic techniques. The rotation-inversion spectrum in the millimeter wave region was measured in this laboratory² leading to the determination of the splitting between the 0⁺ and 0⁻ inversion levels to be 0.369 cm⁻¹. In order to facilitate the observation of further transitions involving inversion states of H₂NNC we have used the semirigid inverter model³⁻⁴ to calculate the higher inversion energies. The effective inversion potential energy function³⁻⁴ used as input for the calculation was obtained by refining an *ab initio* inversion potential energy function (kindly calculated on our request by Dykstra and Jasien⁵) through a least squares fit to the available experimental data.

THEORETICAL

The Semirigid Inverter Hamiltonian

The semirigid bender model describing large amplitude bending in 3, 4, or 5-atomic chain molecules has been described in detail in a series of papers by Bunker and coworkers⁶⁻⁹ and also in the review by Jensen¹⁰. Its extension to describe inversion motion in formaldehyde-type molecules, the semirigid inverter, is the subject of

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refs³⁻⁴ and the earlier papers by Moule and Rao¹¹ and Kreglewski¹²⁻¹³. The semirigid inverter Hamiltonian for H₂NNC is obtained through a fairly straightforward generalization of the Hamiltonian used in refs³⁻⁴ for formaldehyde-type molecules, and consequently we refer the reader to the publications cited above for details. In this section we give only a brief outline of the model used, particularly stressing the differences between the theory used here and that employed in refs³⁻⁴.

In the semirigid inverter approximation we describe the molecule as performing a large amplitude inversion described by the coordinate ϱ , which is the supplement of the angle between the NN bond and the HNH angle bisector (see Fig. 1). During this motion, the molecule retains a plane of symmetry containing the CNN chain, and the other structural parameters (bond lengths and bond angles) vary with ϱ in such a way that the nuclear potential energy is minimized for each value of ϱ .

The molecule fixed xyz system is located relative to the molecule so that (a) the origin is at the center of mass, (b) the yz plane is the plane of symmetry containing the NNC chain and (c) the z axis forms an angle ε (to be defined below) with the NN bond (see Fig. 1). The expression for the semirigid inverter Hamiltonian is

$$\mathbf{H}_{ir} = \mathbf{H}_{inv} + \mathbf{H}_{rot}^z + \mathbf{H}_{rot}^{xy}, \quad (1)$$

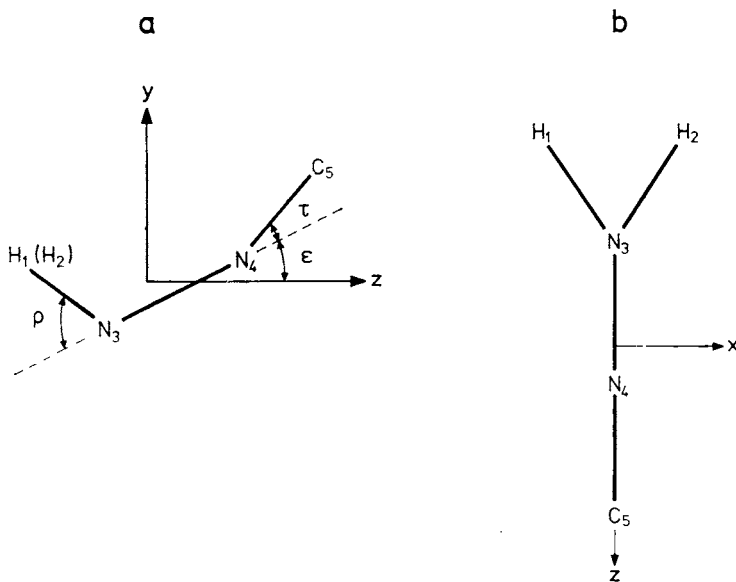


FIG. 1.

The axis system and definitions of the angles ρ , ε , and τ for an inverting H₂NNC molecule. a) The plane of the page is the symmetry plane of the inverting molecule and b) the plane of the page is the xz plane

where

$$\mathbf{H}_{inv} = \frac{1}{2}\mu_{\varrho\varrho}^0 J_{\varrho}^2 + \frac{1}{2}[J_{\varrho}, \mu_{\varrho\varrho}^0] J_{\varrho} - \frac{1}{2}(\mu^0)^{1/4} [J_{\varrho}, \mu_{\varrho\varrho}^0 (\mu^0)^{-1/2} [J_{\varrho}, (\mu^0)^{1/4}]] + V(\varrho), \quad (2)$$

$$\mathbf{H}_{rot}^z = \frac{1}{2}\mu_{zz} J_z^2, \quad (3)$$

and

$$\mathbf{H}_{rot}^{xy} = \frac{1}{2}\mu_{xx} J_x^2 + \frac{1}{2}\mu_{yy} J_y^2 + \frac{1}{2}\mu_{yz}(J_y J_z + J_z J_y), \quad (4)$$

where J_x , J_y , and J_z are the components of the total angular momentum, J_{ϱ} is the momentum conjugate to ϱ , and $V(\varrho)$ is the effective inversion potential energy function. The 4×4 $\mu_{\alpha\beta}$ matrix ($\alpha, \beta = x, y, z$, or ϱ) is the inverse of the 4×4 $I_{\alpha\beta}$ matrix whose elements are defined by Eqs (11a)–(11d) of Sarka¹⁴ if we let the summations in these equations extend over the nuclei of the H₂NNC molecule. However, the bond lengths r_{HN} , r_{NN} , and r_{NC} together with the HNH angle α and the NNC angle τ (Fig. 1) are functions of ϱ .

The angle ε (see Fig. 1) is chosen such that $\mu_{x\varrho}$ is zero. It is easily shown by symmetry arguments that $I_{y\varrho} = I_{z\varrho} = 0$, and consequently $\mu_{x\varrho} = 0$ if $I_{x\varrho} = 0$. This condition leads to the following expression for

$$\begin{aligned} \frac{d\varepsilon}{d\varrho} = \varepsilon' = & \{u_1 + u_{13} \cos \varrho + u_{15} \cos (\varrho + \tau) - m_{\text{C}}(m - m_{\text{C}}) r_{\text{NC}}^2 \tau' \\ & - 2m_{\text{H}}m_{\text{C}}r_{\text{HN}}r_{\text{NC}} \cos \frac{\alpha}{2} \tau' \cos (\varrho + \tau) \\ & - m_{\text{C}}(m - m_{\text{N}} - m_{\text{C}}) r_{\text{NN}}r_{\text{NC}}\tau' \cos \tau \\ & - 2m_{\text{H}}(m_{\text{N}} + m_{\text{C}}) \cos \frac{\alpha}{2} (r_{\text{HN}}r'_{\text{NN}} - r_{\text{NN}}r'_{\text{HN}}) \cdot \sin \varrho \\ & - 2m_{\text{H}}m_{\text{C}} \cos \frac{\alpha}{2} (r_{\text{HN}}r'_{\text{NC}} - r_{\text{NC}}r'_{\text{HN}}) \cdot \sin (\varrho + \tau) \\ & - m_{\text{C}}(2m_{\text{H}} + m_{\text{N}}) (r_{\text{NN}}r'_{\text{NC}} - r_{\text{NC}}r'_{\text{NN}}) \cdot \sin \tau \\ & - \alpha' \sin \frac{\alpha}{2} m_{\text{H}}r_{\text{HN}}((m_{\text{N}} + m_{\text{C}}) \cdot r_{\text{NN}} \sin \varrho + m_{\text{C}}r_{\text{NC}} \sin (\varrho + \tau))\} \cdot \\ & \cdot [u_1 + u_3 + 2u_{13} \cos \varrho + 2u_{15} \cos (\varrho + \tau)]^{-1}, \quad (5) \end{aligned}$$

where

$$u_1 = 2m_{\text{H}}(2m_{\text{N}} + m_{\text{C}}) r_{\text{HN}}^2 \cdot \left(\cos \frac{\alpha}{2}\right)^2, \quad (6)$$

$$u_3 = (m_N + m_C)(2m_H + m_N)r_{NN}^2 + 2m_C(m_H + m_N)r_{NC}^2 + 2m_C(2m_H + m_N)r_{NN}r_{NC}\cos\tau, \quad (7)$$

$$u_{13} = 2m_H(m_N + m_C)r_{HN}r_{NN}\cos\frac{\alpha}{2}, \quad (8)$$

and

$$u_{15} = 2m_Hm_Cr_{HN}r_{NC}\cos\frac{\alpha}{2}. \quad (9)$$

In Eqs (5)–(9), m_X is the mass of an X atom, $m = 2m_H + 2m_N + m_C$ is the total mass of the molecule, and a prime (') denotes differentiation with respect to ϱ . To calculate ε at a given value of ϱ we numerically integrate Eq. (5) setting $\varepsilon = 0$ at $\varrho = 0$.

The ϱ dependence of the bond lengths r_{AB} and of the angles α and τ are modelled as

$$r_{AB} = r_{AB}^p + X_{AB}\varrho^2 + Y_{AB}\varrho^4, \quad (10)$$

$$\alpha = \alpha^p + X_\alpha\varrho^2 + Y_\alpha\varrho^4, \quad (11)$$

and

$$\tau = X_\tau\varrho + Y_\tau\varrho^3. \quad (12)$$

The effective inversion potential energy function is chosen as

$$V = a\varrho^2 + b\varrho^4 + c\varrho^6 + d\varrho^8. \quad (13)$$

The quantities r_{AB}^p , X_{AB} , Y_{AB} , α^p , X_α , Y_α , X_τ , Y_τ , a , b , c , and d entering into Eqs (10)–(13) are all adjustable molecular parameters and, together with the atomic masses, they constitute the input for a semirigid inverter calculation of the inversion-rotation energies. We normally determine these parameters by least squares fitting to experimental data.

The diagonalization of the Hamiltonian in Eq. (3) proceeds exactly as described in Section II of ref.³, and the reader is referred to that publication for details. In the Numerov–Cooley numerical integration stage of the calculation, we used 750 integration points in the range from 0 to 2.10 radians. The numerical accuracy thus achieved was 0.0001 cm^{-1} . In the matrix diagonalization stage, it was necessary to include basis functions up to $v_{\max} + 1$ in order to reach convergence for states with $v_{\text{inv}} = v_{\max}$ and $J = 0$ to 5, v_{inv} being the inversion quantum number (analogous to v_4 in formaldehyde³).

Calculation of Inversion Energies

As starting values for the bond lengths of H₂NNC we used the *ab initio* values of Vincent and Dykstra¹. To allow for the effects of zero point stretching vibrations on the bond lengths we added 0.032 Å to r_{HN}^p , 0.008 Å to r_{NN}^p , and 0.008 Å to r_{NC}^p (1 Å = 10⁻¹⁰ m). These changes from r_e to r_0 were obtained from the results available for the diatomic molecules NH, N₂, and CN¹⁵, respectively, as described also in ref.⁴. In the *ab initio* DZP/SCF calculation by Dykstra and Jasien⁵, which they kindly carried out on our request, they optimized the angle α at each value of ϱ and calculated the corresponding electronic energy. By fitting their *ab initio* potential energy points and their α values to the functions given by Eqs (13) and (11), respectively, we obtained starting values for the parameters α^p , X_α , Y_α , a , b , c , and d . The angle τ was assumed to be zero at all values of ϱ . The *ab initio* data provided by Dykstra and Jasien⁵ are given in Table I, and the starting values of the various parameters are included in Table II.

Initially, we used the starting values of the parameters as input for a calculation of the six lowest inversion energies of H₂NNC. The results are included in Table III. It is remarkable that the 0⁺ – 0⁻ splitting is calculated at 0.362 cm⁻¹, only 0.007 cm⁻¹ away from the experimental value².

In order to further improve the calculated inversion energies we have carried out a least squares fit of the parameters of the semirigid inverter to the millimeter wave data obtained by Schäfer and Winnewisser². As input were used all *calculated* transition frequencies in Table 2 of ref.² involving states with $J \leq 5$. We fit to these low J transitions because the semirigid inverter model does not account for centrifugal distortion effects due to the small amplitude vibrations. Each frequency was weighted with $1/\delta^2$, where δ is its estimated standard error taken from Table 2 of ref.². There exist 64 such transitions (24 rotational transitions within the 0⁺ level, 24 rotational transitions within the 0⁻ level and 16 transitions connecting the 0⁺ and 0⁻ levels), and the standard deviation of the fit to them was 6.3 MHz = 0.0002 cm⁻¹. In the fit, we found that we could usefully vary the parameters r_{HN}^p , r_{NN}^p , α^p , and a . The parameter values obtained are included in Table II, and the inversion energies calculated are included in Table III. The parameters did not change very much in the fit, and consequently the energies obtained with the fitted parameter values are very close to those obtained with the pure *ab initio* values.

Since the experimental input data contain information about one vibrational energy splitting only (the 0⁻ – 0⁺ splitting), we can only determine one effective inversion potential energy function parameter. In the fit described above (Fit I), this parameter was chosen to be a . It is seen from Table II that the term quadratic in ϱ (depending on a) and the term quartic in ϱ (depending on b) are the dominant terms in the effective potential energy function. In order to investigate the effect of the rather arbitrary choice of a as the parameter to vary, we have carried out

TABLE I

Optimized values of the HNH angle α and inversion potential energy function for isocyanamide H_2NNC from the DZP/SCF *ab initio* calculation by Dykstra and Jasien

ϱ/deg	α/deg	$E/\text{a.u.}$	ϱ/deg	α/deg	$E/\text{a.u.}$
0	125.2	-147.8642573	45	114.2	-147.8723953
5	125.1	-147.8643846	55	110.5	-147.8737608
10	124.6	-147.8647645	60	108.8	-147.8735319
15	123.8	-147.8653911	65	107.4	-147.8724104
25	121.3	-147.8673144	75	105.4	-147.8666101
35	117.9	-147.8698677	90	105.3	-147.8461742

TABLE II

Parameter values of the semirigid inverter for H_2NNC

Parameter	<i>Ab initio</i> ^a	Fit I ^b	Fit II ^c
$r_{\text{HN}}^p/\text{\AA}$	1.029	1.018981(85) ^d	1.01826(19)
$X_{\text{HN}}/\text{\AA rad}^{-2}$	0.0	0.0 ^e	0.0
$Y_{\text{HN}}/\text{\AA rad}^{-4}$	0.0	0.0	0.0
$r_{\text{NN}}^p/\text{\AA}$	1.360	1.383448(18)	1.384265(82)
$X_{\text{NN}}/\text{\AA rad}^{-2}$	0.0	0.0	0.0
$Y_{\text{NN}}/\text{\AA rad}^{-4}$	0.0	0.0	0.0
$r_{\text{NC}}/\text{\AA}$	1.177	1.177	1.177
$X_{\text{NC}}/\text{\AA rad}^{-2}$	0.0	0.0	0.0
$Y_{\text{NC}}/\text{\AA rad}^{-4}$	0.0	0.0	0.0
α/rad	2.183	2.17091(18)	2.17546(63)
X_α/rad^{-1}	-0.355	-0.355	-0.355
Y_α/rad^{-3}	0.088	0.088	0.088
$a/\text{cm}^{-1} \text{rad}^{-2}$	-4 320	-4 313.73(35)	-4 320
$b/\text{cm}^{-1} \text{rad}^{-4}$	2 226	2 226	2 218.41(62)
$c/\text{cm}^{-1} \text{rad}^{-6}$	0	0	0
$d/\text{cm}^{-1} \text{rad}^{-8}$	31	31	31
ϱ_e^f/deg	55.8	55.7	55.8
H^g/cm^{-1}	2 070	2 064	2 077

^a Obtained from the *ab initio* results of Dykstra and Jasien⁵. ^b Obtained by fitting to the experimental data of Schäfer and Winnewisser² varying the a parameter (Eq. (13)). ^c Obtained by fitting to the experimental data of Schäfer and Winnewisser² varying the b parameter (Eq. (13)). ^d Quantities in parentheses are standard errors in units of the last digit given. ^e Parameters, for which no standard error is given, were constrained in the least squares fit. ^f Equilibrium ϱ value calculated from a , b , c , and d . ^g Barrier to planarity calculated from a , b , c , and d .

another fit (Fit II) varying r_{HN}^p , r_{NN}^p , α^p , and b . The standard deviation of this fit was $9.8 \text{ MHz} = 0.0003 \text{ cm}^{-1}$. The parameter values obtained are included in Table II and the energies calculated with these parameter values are included in Table III. It is seen that essentially the same inversion energies are obtained from the two fits. The effective inversion potential energy function obtained in Fit I is shown in Fig. 2.

Even though the "Fit I" and "Fit II" energies of Table III are obtained from parameter values determined from fitting to experimental data, they nevertheless depend heavily on the *ab initio* results of Dykstra and Jasien⁵ since the experimental input data² only contain information about one inversion energy splitting as mentioned above. If we use the "Fit I" energies of Table III as a reference point, they of course depend on the *ab initio* values of the structural parameters (r_{NC}^p etc.) that were not varied in the fit, and on the *ab initio* values of the potential energy para-

TABLE III

Inversion energies of H₂NNC (in cm^{-1}) calculated using the semirigid inverter Hamiltonian

Energy	<i>Ab initio</i> ^a	Fit I ^b	Fit II ^c
0 ⁺	0.0	0.0	0.0
0 ⁻	0.36	0.37	0.36
1 ⁺	874.26	874.07	878.10
1 ⁻	891.96	892.07	895.97
2 ⁺	1 546.94	1 545.06	1 553.04
2 ⁻	1 741.31	1 741.41	1 749.00

^a Calculated using *ab initio* parameter values from Table II. ^b Calculated using "Fit I" parameter values from Table II. ^c Calculated using "Fit II" parameter values from Table II.

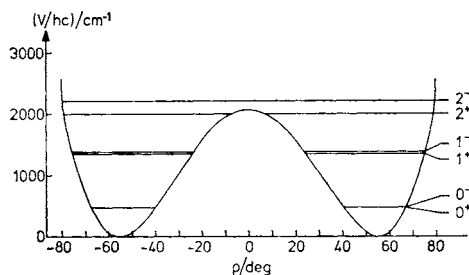


FIG. 2

The effective inversion potential function and inversion energy levels in the small amplitude vibrational ground state of isocyanamide H₂NNC

meters b and d . The most important parameter in this context is b since the excellent fit to the rotational structure in the 0^+ and 0^- states indicates that the structural parameters are essentially correct, and since d is very small. We have investigated the dependence of the inversion energies on b by carrying out two fits analogous to Fit I (i.e., varying r_{HN}^p , r_{NN}^p , α^p , and a). In the first of these fits, b was constrained to the value $b = 2\,003\text{ cm}^{-1}\text{ rad}^{-4}$, 10% lower than the *ab initio* value used in Fit I, and in the second fit, b was constrained at $b = 2\,449\text{ cm}^{-1}\text{ rad}^{-4}$, 10% higher than the *ab initio* value. The two fits were somewhat poorer than Fit I, the “-10%” fit having a standard deviation of $36.5\text{ MHz} = 0.0012\text{ cm}^{-1}$, and the “+10%” fit having a standard deviation of $32.1\text{ MHz} = 0.0011\text{ cm}^{-1}$. The values of r_{HN}^p , r_{NN}^p , and α^p resulting from the two fits are very close to those obtained from Fit I, but in the “-10%” fit, we determine $a = -3\,947.0(10)\text{ cm}^{-1}\text{ rad}^{-2}$, whereas the “+10%” fit yields $a = -4\,676.6(32)\text{ cm}^{-1}\text{ rad}^{-2}$ (quantities in parentheses are standard errors in units of the last digit quoted). The inversion energies obtained from the parameters determined in the two fits are given in Table IV. It is seen that even though the inversion energies themselves change considerably when b changes the $n^+ - n^-$ splittings are much less affected. Consequently, one could hope that the predicted values for these splittings would be sufficiently accurate to allow millimeter wave and far infrared spectra to be assigned.

SUMMARY AND CONCLUSION

Based on an *ab initio* calculation by Dykstra and the experimental data by Schäfer and Winnewisser² we have used the semirigid inverter model for H_2NNC to calculate

TABLE IV
Dependence of the inversion energies on the potential energy parameter b (Eq. (13))

Energy	Fit I ^a		$1.1 \cdot b^b$		$0.9 \cdot b^c$	
0^+	0.00 } 0.37 }	0.37 ^d	0.00 } 0.35 }	0.35	0.00 } 0.37 }	0.37
1^+	874.07 } 892.07 }	18.00	924.67 } 942.06 }	17.39	819.89 } 838.06 }	18.17
2^+	1 545.06 } 1 741.41 }	196.35	1 640.56 } 1 837.72 }	197.16	1 444.38 } 1 636.72 }	192.34

^a Energies obtained with the “Fit I” parameters of Table II. ^b Energies obtained with parameters determined in the “+10%” fit (see text). ^c Energies obtained with parameters determined in the “-10%” fit (see text). ^d $n^+ - n^-$ splittings.

higher inversion energies of this molecule. It is hoped that these calculations will allow further transitions of H₂NNC to be assigned.

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REFERENCES

1. Vincent M. A., Dykstra C. E.: *J. Chem. Phys.* **73**, 3838 (1980).
2. Schäfer E., Winnewisser M.: *Ber. Bunsenges. Chem. Phys.* **86**, 780 (1982).
3. Jensen P., Bunker P. R.: *J. Mol. Spectrosc.* **94**, 114 (1982).
4. Jensen P., Bunker P. R.: *J. Mol. Spectrosc.* **95**, 92 (1982).
5. Dykstra C. E., Jasien P. G.: Unpublished results (1982).
6. Bunker P. R., Landsberg B. M.: *J. Mol. Spectrosc.* **67**, 374 (1977).
7. Bunker P. R., Winnewisser B. P., Landsberg B. M.: *J. Mol. Spectrosc.* **74**, 9 (1979).
8. Bunker P. R.: *J. Mol. Spectrosc.* **80**, 422 (1980).
9. Jensen P.: *J. Mol. Spectrosc.* **101**, 422 (1983).
10. Jensen P.: *Comp. Phys. Rep.* **1**, 1 (1983).
11. Moule D. C., Ramachandra Rao Ch. V. S.: *J. Mol. Spectrosc.* **45**, 120 (1973).
12. Kreglewski M.: *J. Mol. Struct.* **55**, 135 (1979).
13. Kreglewski M.: *J. Mol. Struct.* **60**, 105 (1980).
14. Sarka K.: *J. Mol. Spectrosc.* **38**, 545 (1971).
15. Huber K. P., Herzberg G.: *Constants of Diatomic Molecules*. Van Nostrand-Reinhold, New York 1979.