Appl. Phys. B 48, 257–260 (1989)

Applied Physics B Photophysics and Laser Chemistry

An Explanation of the Direction of the Relaxation in the HCN Gas Microwave Laser, and a New Assignment of Further Laser Lines Along the Path of Internal Vibrational Energy Redistribution*

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Received 2 November 1987/Accepted 15 July 1988

Abstract. We assume a direct connection between the shape of the anharmonic potential energy surface of a molecule and its internal vibrational energy redistribution. In the case of HCN there is a transition from convex to concave behaviour of the equipotential lines in the fundamental range. This explains the existence of the known laser transitions in the line systems of 11^10–04^00 and 12^00, 12^20–05^10, and leads to the assignment of further lines at 35.211, 18.335, and 14.792 cm^{-1} to 10^00–03^10, 03^30 and the line at 12.928 cm^{-1} to 20^00–06^00. For the pure IVR transition we assume symmetry selection $\pm \leftrightarrow \pm$ without a Coriolis resonance.

PACS: 82.20Rp, 42.55Hq, 31.10

The HCN laser discharge system was empirically discovered in 1964 by Gebbie et al. [1]. It has been shown [2–6] that six HCN laser transitions involve the 11^10 and 04^00 states of HCN and four involve the 12^00, 12^20, and 05^10 states. For a long time this was essentially the last word on the subject. But there still remain at least 13–18 unassigned HCN laser transitions [7–10]. In the known assignments the stimulated emission is attributed to a mechanism based on a Coriolis perturbation between rovibrational levels. In a new fit of the anharmonic potential energy surface (PES) of the normal modes of HCN [11] (Fig. 1), which differs particularly in the coupling of the bending vibration ν_2, we have a guide to understanding these assignments and to interpreting some more of the well-known lines of the HCN microwave laser. We show that the laser transitions can be explained in connection with a process of internal vibrational energy redistribution (IVR) [12]. The surprising high coupling between the bending mode and the CN stretch has recently been obtained by Dunn et al. [13] in ab initio CI calculations.

1. The PES and the Vibrational Modes

The representation of the vibrational energy in cm^{-1} in dimensionless normal coordinates is

$$E=\frac{1}{2}\sum_{i=1}^{3}\omega_i(q^i)^2+\frac{1}{6}\sum_{ijl}^{3}k_{ijl}q^iq^jq^l+\frac{1}{24}\sum_{ijkl}^{3}k_{ijkl}q^iq^jq^kq^l\,.$$

All terms containing odd powers of (q^2) are identically equal to zero for a linear molecule from symmetry considerations. Using the anharmonic constants from [11] in the energy formula we get Fig. 1 as the intersection of the bending mode axis q^2 and the stretching axis q^1, which mainly represents the CN stretch. The ν_1 overtones are vibrations of the system

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* Presented in part at the 2nd International Symposium on Elementary Processes and Chemical Reactivity, Liblice, September 7–11, 1987

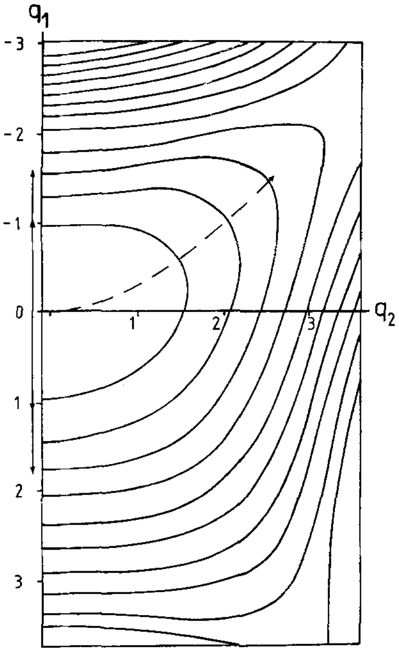

Fig. 1. Potential energy surface of HCN [11]; normal mode section q^2 (bend) and q^1 (CN stretch) at $q^3=0$, equipotential lines at intervals of 1000 cm^{-1}. The full arrows indicate ν_1 and the zero energy of ν_1; the dashed arrow indicates the valley for $3\nu_2$

along the q^1 axis. They are unstable because of missing "side walls" in their compression phase for $q^1<0$. Combination modes 11^10 or 12^00 are more stable, but the most global stability arises for pure bending states because they lie on strongly convex regions on the PES with respect to their turning points. The states of the upper laser levels contain ν_1 components. The ν_1 vibration is formally stable when viewed only along the normal mode direction, but unstable from the global situation on the PES (Fig. 1). Thus, the final states of laser transitions are bending states, which are more stable but relax more rapidly in their overtone ladder [6] because of the curvilinear valley for the bending wave functions. A level inversion occurs, which is a prerequisite for every laser process.

Table 1. Rotational constants and band centers of $H^{12}C^{14}N$, in cm^{-1}

State	B_v	V_0
10^00	1.4681423	2096.855
03^10	1.4895746	2113.463
03^30	1.4878670	2143.795
20^00	1.4580034	4173.100
06^00	1.5024780	4185.889

2. Calculation of Rotational Lines of Interest

The rotational contribution to the energy of a molecular state is

$$E_{\mathrm{rot}}=B_v[J(J+1)-l^2] \pm\tfrac{1}{2}q_vJ(J+1)-D_v[J(J+1)-l^2]^2 +H_v[J(J+1)-l^2]^3\,, \tag{1}$$

where B_v is the rotational constant, D_v the distortion constant and q_v the constant of the l-type doubling in the simplest bending case ($v_2=1$ and $l=1$); q_v is itself a function of J. The + or − signs in q_v give the e and f lines of a degenerate bending state [14]. For higher bending states, matrix elements and formulae giving l-type doubling and further splittings by l-type resonance are published in [15–18] (see also [19]). We have used the constants given there, as well as the fitted equilibrium rotational constant expansion, to compute some B_v from [Ref. 6a, Eq. (37)], see Table 1. In the l-type doubling constant we use the ansatz

$$q_v=q_v^0-q_v^JJ(J+1)+q_v^{JJ}J(J+1)^2$$

with

$$q_v^0=0.007376935 +(7.0048v_3+11.0793v_2-0.2001v_v)\times10^{-5}\,,$$

$$q_v^J=[8.3224241+0.543709(v_2+1)/2]\times10^{-8}\,,$$

$$q_v^{JJ}=1.2\times10^{-12}\,.$$

The other constant expansions are

$$D_v=[2.9085153 +(-0.028v_3+0.071v_2+0.007v_1)]\times10^{-6}\,,$$

$$H_v=3.0\times10^{-12}\,,$$

$$\delta^J=\delta-0.00081J(J+1)+3.1\times10^{-9}[J(J+1)]^2\,.$$

These constants are results of different fitting procedures to reproduce the large collection of experimental data in the cited papers. Units of cm^{-1} are used, the conversion being 1 cm^{-1} = 29979.2456 MHz.

3. The System 11^10–04^00

The band centers of the two line systems in question differ by 2.62 cm^{-1} [2]. A slight difference in the rotational constants leads to a level crossing at the rotational quantum number $J=10$ of both states, connected with a Coriolis perturbation of this level [2–6]. In the range of this level crossing we have the following standard situation of a microwave laser: The two systems have nearly the same value of the rotational transition $J\to J-1$ but their corresponding rovibrational states may have quite different thermodynamic population probabilities. Thus if we induce rotational emission we can observe a channel of rapid and intense energy flow from the globally unstable to the more stable state. In the system in question we have laser transitions around 337 µm. (The physics of this laser is treated further in a series of papers [20]). Hence, the underlying reason for the transitions is a great difference in the population probabilities of the initial and final states. The Coriolis perturbation of the included levels is an aspect of the level crossing; it is not the driving force for the laser. Of course, if the global instability of a ν_1 rotational level is additionally perturbed by a resonance then this should accelerate the decay.

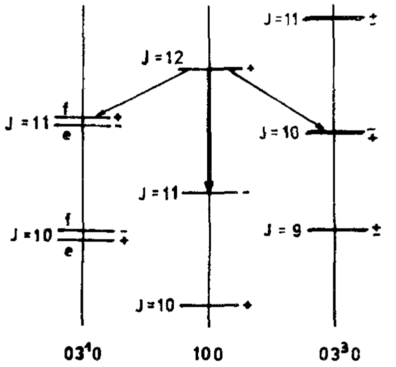

Fig. 2. Energy level diagram of HCN. The arrows indicate laser transitions that have been reported

4. The System 10^00–03^10, 03^30

Behind the known 11^10–04^00 laser there is the pure state 10^00, which has been the source of a confusing discussion in the literature due to its intensity anomaly in infrared absorption (see [12] and references therein). Recently we proposed an elucidation of the intensity anomaly at the beginning of the R branch up to $J \approx 11$ of ν_1 by IVR [12], explaining the very intense Q branch of the $3\nu_2^1$ band. Consequently, the occupation of the rotational levels in the state 10^00 up to $J = 11$ is lower than that of rotational states with higher J. Thus, a level inversion in the lower 10^00 rotational ladder has to be assumed, leading to relaxation phenomena. The pure rotational quantum of 10^00, $J = 12 \rightarrow J = 11$, is calculated to be 35.215 cm^{-1}, differing by only 0.004 cm^{-1} from a reported laser transition whose error bar is ± 0.01 cm^{-1} [21].

On the other hand, the instability of the 10^00 state leads to a redistribution of its vibrational energy through a quantum mechanically possible channel to a bending state 03^l0 [12]. Around $J = 12$ a level crossing of the known kind does not exist, but a possible perturbation may increase with J by increasing Coriolis forces of the 10^00 state, leading to a direct decay of this loose state without the action of a Coriolis resonance. If we shift the calculated levels of (1) for 10^00, $J = 12$ by -0.004 cm^{-1}, for 03^30, $J = 10$ by $+0.007$ cm^{-1} and for 03^10, $J = 11$ by -0.008 cm^{-1}, which is within the error limit ± 0.01 cm^{-1} [21], we get three level differences exactly equal to three known laser transitions (Fig. 2):

$$10^00,\ J=12 \begin{cases} \xrightarrow{35.211} 10^00, \quad J=11 \\ \xrightarrow{18.335} 03^{3e}0,\ J=10\,. \\ \xrightarrow{14.792} 03^{1f}0,\ J=11 \end{cases} \tag{2}$$

It should be noted that there are mixed violations of selection rules in the proposed transitions. Selection rules work well for absorption of radiation in stable molecules. If the molecule rotates it is constrained in the corset of the angular momentum which is small in frequency but rigorous in action. But, the global unstable rovibrational states ($10^00, J$) aim for an IVR to reach a more stable quantum state, and this decay can enforce an abnormal reorganization of the rotation.

In detail we observe:

- In the line 18.335 cm^{-1} in (2) there are two opposite transitions with $\Delta J = -2$ and $\Delta l = +3$. Thus in the sum all rotational quantum numbers charge by 1. Strange transitions of $\Delta J = \pm 2$ have already been observed in HCN [22]. See [23] for an example in NCO. Likewise, $\Delta l = +3$ transitions have been observed in HCN [24]. In the weak spectroscopic observation of infrared transitions to 03^30 the J lines start with $J = 9$ [20, 24]. Thus, they can be populated in part by the assumed IVR.
- In the line 14.792 cm^{-1} in (2) we have a selection violation by the $+ \leftrightarrow +$ transition. This may be explained by the value of the energy difference of the transition: The assignment $\Delta J = -1$ formally described the difference of the two rotational levels concerned, but the real laser transition is less than half of a ΔJ step of any of the corresponding ladders. The change in the total energy in the course of the IVR is too small to influence the symmetry character. Herzberg [Ref. 25, p. 380] has discussed the possibility of a violation of selection rules in a strong interaction of vibration and rotation: This is in fact the case in the IVR where two states interact strongly in their vibrational structures, affecting the rotational behaviour of both the initial and final states as a vibrational state is redistributed.

5. IVR from 20^00

The state 20^00 is very labile and its infrared absorption spectrum is extremely weak [17, 26]. We understand this on the basis of equipotential line shape of the PES for $2\nu_1$ for $q^1 < 0$, which is clearly concave (Fig. 1). The

20^00 rotational spectrum begins some cm^{-1} before the systems 06^l0 or 13^10 [17]. Thus, up to the rotational quantum number $J=4$ there is no level of these neighbouring systems that could act as a target for a known laser transition. If we accept the more extended selection rule $\Delta J=-2$ with symmetry selection $\pm \leftrightarrow \pm$ then the first possible transition is

$$20^00,\ J=5 \xrightarrow{12.925} 06^00,\ J=3,$$

differing by only $0.003\,\mathrm{cm}^{-1}$ from the reported laser transition $12.928\,\mathrm{cm}^{-1}$. Hence, the extremely unstable vibrational state 20^00 should lase in this line.

6. Discussion

In our laboratory our interest is concentrated on

- the global shape of a PES,
- its stationary points [27] and
- the definition of a reaction coordinate [28],

and the connection of such theoretical tools with the real dynamical behaviour of a reacting molecule. The appearance of IVR is a key opening the door between the word of spectroscopic facts for "stable" molecules and the world of chemical knowledge concerning the rearrangement paths of not so stable parts of molecules. Hence, every kind of IVR should receive our greatest attention.

In general, laser transitions in the microwave region are rotational transitions connected with a simultaneous reorganization of the underlying vibrational state of the molecule. The driving force for such a complicated intramolecular process is a great difference in the global stability of the vibrational states involved. If the region of a normal mode on the PES changes from convex to concave behaviour up the level ladder then the mode loses its stability and tends to release its vibrational energy into a more stable mode. Which actual rotational state is selected to permit the transition is rather a matter of accident. It can be a direct Coriolis resonance of some single rotational levels or the accidental existence of neighbouring rovibrational states that gives a target.

The lasing behaviour in HCN is observed quite early in the fundamental ν_1, giving transitions from pure ν_1 states 10^00 and 20^00 and from combination modes with ν_1 parts. The reorganization of the vibrational states is, in other words, an internal vibrational energy redistribution (IVR). So, with the explanation of some HCN laser transitions which has long been outstanding [8], we get simultaneously a nice simple model of IVR to supplement the infrared part of the same model [12].

Acknowledgement. I thank Doz. Dr. Heidrich for his useful help and comments.

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