Calculation of the Herman–Wallis effect in $\Pi$–$\Sigma$ vibrational overtone transitions in a linear molecule: Comparison with HCN experimental results

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The high sensitivity of cavity ring-down spectroscopy has allowed us to observe a few perpendicular vibrational overtone transitions of HCN in the visible. These transitions display a sizable Herman–Wallis effect, that is an asymmetry in the relative intensities of the $R$ and $P$ branch lines. We have developed a theory for the first-order Herman–Wallis effect based upon using variational vibrational wave functions but treating the vibration–rotation interaction by first-order perturbation theory. In the specific case of perpendicular transitions, the first-order effect is dominated by Coriolis mixing of $\Sigma$ and $\Pi$ overtone states. We used the empirical energy surface by Carter, Mills, and Handy [J. Chem. Phys. 99, 4379 (1993)] restricted to the stretching degrees of freedom. Bending was included by multiplication of these stretching wave functions by harmonic wave functions of the bend. Vibrational transition moments were calculated using a polynomial surface fit to $ab\ initio$ CCSD(T) dipole moment points by Botschwina et al. [Chem. Phys. 190, 345 (1995) and private communication]. We expected that this treatment would be accurate but the calculated Herman–Wallis effect is about one order of magnitude too large. To gain further insight into the poor agreement between theory and experiment, we have calculated the sensitivity of the Herman–Wallis coefficient and of the transition moment to the dipole and energy surface parameters. From this, it appears that the dipole surface, while producing accurate band intensities, could at the same time be inadequate to account for the Herman–Wallis effect. A similar possibility stands for the energy surface, which however is highly constrained by the requirement to fit the observed band origins. © 1996 American Institute of Physics. [S0021-9606(96)01925-3]

I. INTRODUCTION

Vibrational spectroscopy has long been used to study the potential energy and dipole moment functions of polyatomic molecules. Traditional IR studies, however, yield information only about the potential curvature and dipole derivatives near the potential minimum. Study of the overtone spectrum expands the region sampled by the vibrational wave functions and thus gives more global information on the potential and dipole surfaces. However, at the higher energies, the traditional perturbative treatments for dealing with anharmonic effects become suspect, and precise comparisons between theory and experiment requires variational calculations for the vibrational wave functions. Because of the exponential increase of the computational cost of such calculations with the number of vibrational degrees of freedom, triatomic molecules provide the best systems for comparisons.

The most careful comparisons between theory and experiment have been made for the simple hydrides, H$_2$O and HCN. Work in our laboratory has focused on the visible and near-IR spectrum of HCN. Recently, we reported on the extension of the overtone spectrum using the technique of cavity ring down spectroscopy. The observed band origins, rotational constants and isotopic shifts were compared with the variational predictions from an empirical potential energy surface (PES) by Carter, Mills, and Handy (CMH) that was optimized to the previously observed lower energy bands of HCN. The agreement was excellent, with the empirical potential even correctly predicting weak anharmonic resonances of a type not previously observed. In addition, we used the variational wave functions and the $ab\ initio$ dipole moment surface (DMS) by Botschwina et al. to calculate vibrational transition moments and thus integrated band intensities. Again, excellent agreement between theory and experiment was found. Based upon this work, we believed that both the potential and dipole moment surfaces of HCN were well known, at least over a range of stretching coordinates corresponding to over half of the C–H bond dissociation energy.

In addition to the integrated band intensity, one can examine the rotational dependence of the observed line intensities. In the approximation of negligible ro-vibrational coupling, the integrated intensity of individual rotational lines in a molecular vibrational transition can be written in terms of the thermal population distribution and the rotational Hön–London factor. This factor arises from the transformation of the dipole moment operator between the laboratory frame and the molecule-fixed frame (Ref. 8, p. 284). This transformation results in the electric dipole operator being written as a product of the dipole moment as a function of the internal molecular coordinates alone times a direction cosine relating the two reference systems. When one neglects rotation–vibration interactions, the overall wave function can be written as a product of a vibrational part and a rotational part.

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This gives the transition dipole matrix element as a product of a vibrational transition moment independent of the rotational state, and a direction cosine matrix element, which depends upon the rotational quantum numbers and the direction of the dipole moment alone.

If rotation–vibration interaction is not negligible, such a simple factoring of the transition dipole is not possible. The correlations now present between vibrational and rotational motions are reflected in the fact that the ro-vibrational wave function must be written as sums over product terms of zero-order wave functions for the rotations and the vibrations. These different terms in the expansion of the ro-vibrational wave function can lead to interference between the corresponding contributions to the overall transition moment. The lowest-order effect of this type was originally introduced for diatomic molecules by Herman and Wallis (HW). They found that for the fundamental bands, centrifugal distortion resulted in an interference between terms arising from the permanent dipole as well as the dipole derivative. This effect allows spectroscopic determination of the relative directions of these two components, which is not possible from the vibrational band intensity alone. Subsequently, the theory of the HW effect has been extended to polyatomic molecules using the contact transformation method. These treatments use perturbation theory to account for both the anharmonic and the rotation–vibration interactions. As such, they have been restricted to vibrational bands allowed in low order, i.e. fundamentals and low-order combinations and their associated hot bands.

In our spectroscopic study of the visible overtone spectrum of HCN, we found a sizable HW effect in each of the three observed perpendicular bands. These are the $11^15\rightarrow000$ and the $01^16\rightarrow000$ transitions in H$^{13}$CN and the $11^15\rightarrow000$ in the common isotopomer. Only these perpendicular bands where measured mainly because they are approximately two orders of magnitude weaker than the corresponding parallel bands having the same change in stretching quantum numbers. Based upon the above-mentioned success of the PES and DMS in predicting the band intensities, we fully expected that these should be able to predict the observed HW effects as well. We hoped that the effect would be dominated by the interactions of at most a few nearby states, and thus we could use the sign of the observed effect as a test for the relative directions of the vibrational transition moments. In addition to the perpendicular HCN bands we detected in the visible, several low-energy combination bands were recently investigated by Maki et al. who determined both first- and second-order HW corrections to the rigid rotor line strengths. Among these, the results for the fundamental bending transition and another combination band, will also be considered here for comparison to our theoretical values. Note that due to a difference in the definition of the transition moment for a degenerate state, the reported dipole moments values from Maki et al. have been divided by $\sqrt{2}$.

In this paper we use perturbation theory to derive expressions for the HW coefficients in a linear molecule in terms of matrix elements of the dipole moment and of the ro-vibrational coupling Hamiltonian between the vibrational eigenfunctions. Numerical results for the observed perpendicular $\Pi-\Sigma$ overtone transitions in HCN are then calculated using variational wave functions determined by diagonalization of the vibrational Hamiltonian over a large product basis set expansion. Terms in the Hamiltonian are ordered according to the power of the rotational operators, so the Coriolis interactions are part of the first-order perturbation and centrifugal distortion gives corrections in the second order. The physical motivation for this approach is based upon the empirical observation, evident from the spectroscopy of HCN, that while vibrational anharmonic effects are quite strong, each vibrational state has a regular rotational spectrum, with effective rotational constants that vary smoothly with vibrational quantum numbers. This clearly indicates that vibration–rotation interactions lead to energy corrections that have the form predicted by perturbation theory, where such interactions give contributions to the vibrational dependence of the effective rotational constants.

We have worked out the general perturbation formulas for both parallel and perpendicular bands of linear molecules. In keeping with earlier work, we find that the second order for the intensities of lines in the $R$ and $P$ branches are given by $S_1(1+2A_1m+2A_2m^2)$, where $m$ is $J+1$ or $-J$ for the $R$ and $P$ branch, respectively. Here, $S_1$ is connected to the zero-order band intensity $S_0$ by a factor $f$ which is close to unity, $S_1=fS_0$. Our experiments and calculations indicate that the linear HW coefficient $A_1$ (to be written simply as $A$ from now on) dominates for thermally populated rotational levels. The $A_2$ coefficient only has contributions from second and higher orders in our perturbation expansion. In order not to make a long technical digression, the derivation of the first order formulas of both $A$ and $f$ is given in the Appendix. It is interesting to point out that the first-order treatment may still be valid even when the HW effect is quite sizable. This can arise when considering a vibrational band with a particularly weak transition moment, such as one of the perpendicular bands in the visible overtone spectrum of HCN. The reason is simply that a very small mixing-in of excited states with much larger transition moments can produce a very large effect on the intensity. A particularly evident and interesting example is the $001\rightarrow000$ parallel HCN band, which is anomalously weak due to almost perfect accidental cancellation of transition dipole moment and displays a strong HW effect.

Our calculated values of $A$ for the bending fundamental and the other low-lying combination band reported by Maki et al. are in good agreement with the experimental ones. However, for the perpendicular bands in the visible overtone spectrum that motivated our calculation, the calculated effect is about one order of magnitude too large. This result was extremely surprising given the already proven predictive power of both PES and DMS. In order to carefully check our results, the perturbation formulas were derived independently by both authors, and each also wrote independent computer programs to perform the calculations. We found that, in the calculation of the HW effect, there are two contributions that systematically almost quantitatively cancel.
This suggests that a better basis set for the perturbation theory should exist, though we do not know what that basis could be. This cancellation makes it possible, if not likely, that the HW effect be much more sensitive to features of the PES and DMS than the band energies and the integrated intensities. Thus, despite the fact that the PES and DMS of HCN are certainly among the most accurately known, they appear not to give even an order of magnitude estimate for the effect of vibration–rotation interactions on the observed spectroscopic line intensities.

In order to gain further insight into this paradox, we have calculated the sensitivity of both the Herman–Wallis coefficient $A$ and the transition moment to the DMS parameters. We find that the sensitivity of these quantities is quite different, so that it is possible for a DMS to accurately predict the known band intensities while being inadequate to account for the Herman–Wallis effect. We have also calculated the sensitivity to the PES parameters, which similarly shows that the HW effect and the transition intensities are sensitive to different aspects of the potential. However, the PES is subjected to the rather stringent requirement of accurately fitting the band origins and rotational constants. On the other hand, the situation may be considered similar for the DMS, since the polynomial expansion we use has been fit to accurately determined $ab$ initio points. The problem might then lie with the polynomial fit, not with the accuracy of the $ab$ initio calculations themselves. In fact, we will see that our sensitivity analysis suggests that the order of the dipole polynomial surface is not completely “converged” with respect to HW coefficients and intensities. A similar observation holds for the PES polynomial expansion.

An additional source of error is our approximate treatment of bend–stretch interactions in the variational calculations. While we expected this to be an excellent approximation for the low bending excitation states considered here, the existence of near cancellations implies that even a small error could be dramatically amplified in the final result. In the future we hope to eliminate this source of error by repeating our calculations using a full three-dimensional variational calculation that explicitly accounts for bend–stretch anharmonic interactions. In any case, the present results clearly indicate that even subtle effects can provide a radically different insight into our understanding of a well studied molecule.

II. EXPERIMENT

Our data were obtained by cavity ring-down spectroscopy, as described in our previous papers. This is a high-sensitivity, linear, and absolute absorption technique, where the decay rate of pulsed laser light injected into a high-$Q$ optical cavity is monitored while the laser wavelength is tuned. The gaseous sample is kept in the cavity and its weak absorption features produce changes in the light decay rate. The gaseous sample is kept in the cavity and its weak absorption features produce changes in the light decay rate. To quantify the sensitivity of the technique, one can introduce an “effective absorption path length,” proportional to the decay rate constant. The effective absorption lengths for the $11^1 5\rightarrow 000$ and $01^1 6\rightarrow 000$ spectra in the H$_3$CN isotopomer were 42 and 60 km, respectively (we follow the HCN normal mode labeling convention $n_{CN}$, $n_{bend}$, $n_{CH}$). It can be seen in Fig. 1 that as a result of the HW effect, line intensities in these bands are substantially weaker in the $P$
branch, which is partly obscured by the strong $Q$ branch progression. In fact, since the Hön–London factors are twice as large in the $Q$ branch as in the $P$ and $R$ branches (which are nearly the same size), the $R$ branch is clearly enhanced relative to the $Q$ branch. Unfortunately, we have observed only one other perpendicular band, that of the $11^{15}→000$ transition of the common $1$-$1$-$14$ isotopomer.

In Fig. 2 we plot the line intensities obtained by fitting with independent Voigt profiles each line in the $11^{15}→000$ and $01^{16}→000$ HCN bands, using a procedure that works well even for strongly blended lines. The population and Hön–London factors have been divided out, and the line intensities are plotted as a function of $m$ ($=J+1$ or $=J$ in the $R$ or $P$ branch, respectively). Notice that, due to the large

\[ \Delta B \text{ of these high overtones, many of the } Q \text{ branch lines could be resolved and fitted separately, yielding accurate intensities also for the } Q \text{ branch. A fit with } S_1(1+Am)^2 \text{ is shown in the same figure, which reproduces the HW } J\text{-dependence to within experimental errors. According to the HW theory, this fitting form is accurate to first order in the vibration–rotation interaction and in the case of fundamental infrared bands of linear molecules, the } A \text{ coefficient has been given in terms of molecular parameters.}^{15,12} \text{ The } A \text{ values from these fits are reported in Table I, where they are compared with our theoretical values. In the same table we also compare the transition moments for the same bands. The values by Maki } et al. \text{ have been divided by } \sqrt{2} \text{ due to different definitions of the transition moment for a degenerate state. In fact, to relate the observed absorption band intensity } I \to \text{ to the transition dipole moment } \mu, \text{ we use the definition given in Ref. 16. In this definition the degeneracy } g \text{ of the upper level is explicitly eliminated: } \mu(\text{Debye}) = 0.6311(I(\text{km/mol})/\nu_0(\text{cm}^{-1}))/g, \text{ where } \nu_0 \text{ is the transition band origin. On the other hand, the definition used by Maki } et al. \text{ in Ref. 12 implicitly includes the degeneracy factor into the transition moment } \mu. \text{ The difference simply reflect whether one is interested in the vibrational transition moment to one of the } (x,y) \text{ polarized bending states (as we are here), or to one of the states of } e \text{ or } f \text{ symmetry, where for a given rotational branch only one is allowed.}

III. THEORY

In the following we will consider the zero-order separable Hamiltonian $H_0$ of the vibrating rigid-rotor, perturbed by vibration–rotation interaction, given by the Coriolis coupling $H_c$ and the centrifugal distortion $H_d$. The mixing of the zero-order eigenstates induced by $H_d$ is on the order of the square of that induced by $H_c$, so it can be neglected.

### Table I. Comparison of experimental and calculated transition moments and HW factors.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\sqrt{S_1}$ (Debye)</th>
<th>$A$</th>
<th>$\sqrt{S_1}$ (Debye)</th>
<th>$f$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$01^{10}→000$</td>
<td>0.134(1)</td>
<td>$6.73(4)×10^{-4}$</td>
<td>0.141</td>
<td>1.00</td>
<td>$5.07×10^{-4}$</td>
</tr>
<tr>
<td>$01^{11}→000$</td>
<td>$4.51×10^{-3}$</td>
<td>$-1.37(11)×10^{-2}$</td>
<td>$9.77×10^{-3}$</td>
<td>1.51</td>
<td>$-0.58×10^{-2}$</td>
</tr>
<tr>
<td>$11^{15}→000$</td>
<td>$1.2×10^{-6}$</td>
<td>0.0109(14)</td>
<td>$1.60×10^{-6}$</td>
<td>0.642</td>
<td>0.0778</td>
</tr>
<tr>
<td>H$^{13}$CN:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$01^{10}→000$</td>
<td>0.1336(2)</td>
<td>$2.96(20)×10^{-4}$</td>
<td>0.140</td>
<td>1.00</td>
<td>$4.98×10^{-4}$</td>
</tr>
<tr>
<td>$01^{11}→000$</td>
<td>$6.55×10^{-3}$</td>
<td>$-0.84(5)×10^{-2}$</td>
<td>$9.88×10^{-3}$</td>
<td>1.49</td>
<td>$-0.56×10^{-2}$</td>
</tr>
<tr>
<td>$11^{15}→000$</td>
<td>$8.47×10^{-7}$</td>
<td>0.0091(17)</td>
<td>$1.51×10^{-7}$</td>
<td>0.631</td>
<td>0.0808</td>
</tr>
<tr>
<td>$01^{16}→000$</td>
<td>$1.07×10^{-6}$</td>
<td>0.0281(16)</td>
<td>$1.53×10^{-6}$</td>
<td>0.726</td>
<td>0.0903</td>
</tr>
<tr>
<td>HC$^{13}$N:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$01^{10}→000$</td>
<td>0.1360(1)</td>
<td>$5.07(55)×10^{-4}$</td>
<td>0.141</td>
<td>1.00</td>
<td>$4.92×10^{-4}$</td>
</tr>
</tbody>
</table>
While this is expected on the basis of general arguments, the expressions in the Appendix have been derived keeping the $H_d$ first-order contribution. We verified numerically that all of the $H_d$ mixing coefficients are indeed on the order of the square of those due to $H_c$. An additional reason for neglecting the centrifugal distortion is that the contribution it gives to the transition moment is of perpendicular type, while that due to $H_c$ is parallel and therefore has much larger magnitude. As discussed in the Appendix however, in the case of parallel transitions this last situation is reversed, and the mixing due to $H_d$ cannot be so easily neglected.

The effect of Coriolis coupling is to mix a small amount of $\Sigma$ and $\Delta$ character into the zero-order $\Pi$ states, and some $\Pi$ character into the zero-order $\Sigma$ states. When calculating the intensity of a $\Pi\rightarrow\Sigma$ transition (proportional to $|\langle\Pi|\mu|\Sigma\rangle|^2$), the $\langle\Sigma|\mu|\Sigma\rangle$ and $\langle\Pi|\mu|\Pi\rangle$ dipole–moment matrix elements from the mixing interfere with the zero-order term $\langle\Pi|\mu|\Sigma\rangle$. Mixing of $\Delta$ character, on the other hand, produces no first-order effect on the intensities because $\langle\Delta|\mu|\Sigma\rangle$ is zero. Since the mixing depends on the rotational quantum number, the intensities are $J$ dependent, as required by the HW effect. The $\Sigma\rightarrow\Pi$ and $\Pi\rightarrow\Sigma$ transition moment can be very large relative to the zero-order $\Pi\rightarrow\Sigma$ moment—which is obvious if one considers that the overtone spectrum of HCN is dominated by parallel bands—therefore even a small mixing can produce sizable effects. The largest mixing coefficients that we obtain are on the order of $10^{-4}$ for Coriolis coupling ($10^{-8} \times J^2$ for the centrifugal distortion), confirming that a first-order treatment is appropriate for thermally populated levels ($J \sim 10$).

By symmetry, the Coriolis mixing with $\Sigma$ vibrational states (which for triatomic molecules must be of $\Sigma^+$ symmetry) and the associated intensity effect can only involve $e$ sublevels of the upper $\Pi$ state, which are those reached by $R$ and $P$ branches in $\Pi \rightarrow \Sigma$ transitions. This gives the above intensity dependence $I_R(J) \sim f S_0 (1 + A_m A_n)^2$. On the other hand, the $Q$ branch transitions contains the $f$ sublevels of the $\Pi$ state, and first-order Coriolis interaction can mix these sublevels only with $\Delta$ states, with no first-order change in the line intensities. However, mixing of the lower $\Sigma$ state with $e$ sublevels of other $\Pi$ states gives a contribution to the $Q$ branch transition intensities, with the same global multiplicative factor $f$ as the $R$ and $P$ branches, and a lowest-order squared $J$ dependence $I_Q(J) \sim f S_0 (1 + A_Q J(J+1))^2$, where $A_Q$ depends only on $H_d$ and is therefore much smaller than $A$.

For our calculations, the vibrational HCN eigenfunctions of $H_0$ were obtained using the very accurate empirical PES by Carter, Mills, and Handy (see Table II). Due to computational limitations, we treated variationally only the stretching degrees of freedom. The CMH PES is given as a truncated series in Morse coordinates $[1 - \exp(-\alpha(\nu-\nu_0))]$ for the bond stretches, and in even powers of the angle for the bend. Therefore, as convenient basis functions for diagonalization of the stretch-only problem, we used products of bound Morse eigenfunctions for the CH and CN bond coordinate. All matrix elements of the position and momentum operators in the Morse problem can be evaluated analytically. This is very convenient in setting up both the matrix $H_0$ to be diagonalized and to determine the matrices of all other operators that enter the calculation. Only product basis states with energy expectation value below a maximum of 40 000 cm$^{-1}$ were used, giving a basis set of about 140 states. We checked that all the quantities of interest are fully converged by comparing with results obtained using a basis that contains all bound Morse product states with energy expectation value below 60 000 cm$^{-1}$ (~400 wave functions). A first-order anharmonic correction accounting for excitation of the bend is included in the calculation, following the method introduced by Botschwina and modified for a local mode calculation by Smith et al. This results in slightly different effective PESs for the $\Sigma$ and $\Pi$ states, and thus slightly different vibrational wave functions for the stretching coordinates. The energies that we obtain are very close to the experimental values: within 5 cm$^{-1}$ for the $\Sigma$ and 10 cm$^{-1}$ for the $\Pi$ states. The software is a modified version of the code written by Dr. Alice M. Smith.

As is shown later below [see Eqs. (A17), (A26), and (A27)], calculation of the HW effect requires the matrix elements of two operators ($K$ and $U$ in the notation of the Appendix, with $H_e = U/K$) which control the mixing coefficients among the zero-order states. These are simple functions of the position and momentum operators for the molecular degrees of freedom. The same holds for the dipole moment, which is a power series (Table III) in the bond coordinates and bend angle, obtained by fit to ab initio CCSD(T) points by Botschwina et al. The parallel and perpendicular components of the dipole operator are referred to the Eckart axis system. They are thus not isotopically invariant, but we will ignore the small changes in these axes produced by isotopic change of the heavy atoms. It may be the case that this approximation is responsible for our underestimate of the experimentally observed isotopic dependence of the HW effects.

We use a harmonic approximation for the bending wave functions, and thus since the Coriolis coupling is linear in the

| $\alpha$(CH) | 1.886 155 | V(1,3) | $-1.041 680 \times 10^{-1}$ |
| $\alpha$(CN) | 2.244 842 | V(0,4) | $6.045 185 \times 10^{-2}$ |
| $\chi^{\text{rad}}$ | $-18.137$ | V(5,0) | $8.512 691 \times 10^{-3}$ |
| $\chi^{\text{rad}}$ | $-3.952$ | V(4,1) | $1.533 951 \times 10^{-2}$ |
| $\chi^{\text{ang}}$ | 2.451 | V(3,2) | $-1.774 082 \times 10^{-1}$ |
| V(2,0) | 0.878 188 835 | V(2,3) | $3.342 118 \times 10^{-1}$ |
| V(1,1) | $-0.047 238 716$ | V(1,4) | $-7.611 916 \times 10^{-2}$ |
| V(0,2) | 1.852 201 754 | V(0,3) | $-7.360 404 \times 10^{-2}$ |
| V(3,0) | 1.171 049 $\times 10^{-3}$ | V(6,0) | $4.958 699 \times 10^{-2}$ |
| V(2,1) | $-2.110 56 \times 10^{-2}$ | V(5,1) | $-2.160 302 \times 10^{-2}$ |
| V(1,2) | $-2.064 893 \times 10^{-3}$ | V(4,2) | 0 |
| V(0,3) | $-3.669 781 \times 10^{-3}$ | V(3,3) | $4.257 051 \times 10^{-2}$ |
| V(4,0) | 7.379 604 $\times 10^{-2}$ | V(2,4) | 0 |
| V(3,1) | $-3.475 433 \times 10^{-2}$ | V(1,5) | $2.886 079 \times 10^{-2}$ |
| V(2,2) | $-4.567 845 \times 10^{-3}$ | V(0,6) | $-1.535 145 \times 10^{-2}$ |

TABLE II. Force constants for the expansion in Morse coordinates of the empirical HCN PES by Carter, Handy, and Mills (Ref. 6). The equilibrium structure is given by $r_e$(CH) = 1.065 01 Å and $r_e$(CN) = 1.153 24 Å. All values are in units of $\text{cm}^{-1}$. The Morse range parameters $\alpha$(CH) and $\alpha$(CN) which are in units of Å$^{-1}$.
bending coordinate and momentum, we get the selection rule that states are coupled that differ by only ±1 quanta in the bending mode. Since the states we are considering all have 0 or 1 quanta of bending excitation, the only bending matrix elements we need are those between the ground and the first excited bending states. These matrix elements are needed for the matrix of the perpendicular dipole moment $\mu_x$ and the $K$ matrix, as in Eq. (A27). As mentioned earlier, we use analytical expressions for Morse oscillator matrix elements of operators involving the coordinates and momenta of the CN and CH bond local modes. By using matrix inversion, product, and addition, we can calculate the $K$, $U$, $\mu_x$, and $\mu_z$ matrices. Then, to transform these to the diagonal representation of $H_0$, we use the matrix expressing the eigenfunctions of $H_0$ in terms of the product wave functions. This orthogonal transformation matrix is obtained from the diagonalization of the vibrational Hamiltonian. For improved accuracy, we use two transformation matrices where they are needed (as for $\langle \Pi | K | \Sigma \rangle$): one for the $\Sigma$ eigenfunctions, calculated from the effective PES with no bend excitation, and one for the $\Pi$ basis, from the effective PES with one quantum of bending excitation.

It is quite informative to consider the size of the transition moment induced by the Coriolis mixing. In Fig. 3 we plot the terms

$$a_i = \frac{s_{ij} \langle \Sigma | \mu_x | \Pi \rangle}{\langle \Pi | \mu_x | \Sigma \rangle},$$

$$b_i = -\frac{\langle \Pi | \mu_x | \Sigma \rangle s_{ij}}{\langle \Pi | \mu_x | \Sigma \rangle},$$

$$s_{ij} = \frac{\langle \Pi | J M | H_0 | \Sigma \rangle}{\sqrt{J(J+1)}}$$

with $j=0$ and $k=31$ for the $1115\rightarrow000$ transition. These appear in the definition of $A$ and $f$ in Eq. (A22). Coriolis mixing of the upper $|\Pi_{k=31}\rangle$ state with $|\Sigma_i\rangle$ produces the $a_i$ term, which is therefore associated with the $|\Sigma_{0}\rangle$ state with $|\Pi_i\rangle$, and has an associated transition moment $\langle \Pi_{11}^+ | \mu_x | \Pi_i^\dagger \rangle$. We also plot the running sum of these terms, which converges to the $A$ coefficient [apart from the factor $1/\sqrt{J}$ of Eq. (A22)]. The interesting point is that the largest values of $a_i$ and $b_i$, due to the permanent dipole moment (from the matrix elements $\langle \Sigma_0 | \mu_x | \Sigma_0 \rangle$) and $\langle \Pi_{11}^+ | \mu_x | \Pi_{11}^\dagger \rangle$, almost cancel each other. The same holds for the other terms: each $a_i$ has a correspondent $b_i$ almost opposite in size. This cancellation effect is due to the similarity of $s_{ij}$ to $|\Pi_i \mu_x | | \Pi_i^\dagger \rangle$, and that of $s_{ij}$ to $|\Sigma_i | \mu_x | \Sigma_i \rangle$. The first pair of terms is characterized by “peaks” for the same values of $i$, clustered around $i=k$, while the second pair has the same kind of peak structure around $i=j$. For $j=31$ (1115 state), we find that the largest values correspond to the $\Sigma$ states 104, 105, and 106. The similarity of these terms must be due to the operator $U(-I^{-1})$ being almost diagonal, so that $s_{ij}$ is mainly determined by $K$, which ---like $\mu$--- is

![FIG. 3. Plot of the terms $a_i$ (crosses), $b_i$ (empty squares), and their running sums (full dots), for the case of the 1115→000 transition ($k=31$). These quantities are defined explicitly in Eq. (1). They appear in the definition of $f$ and their sum in practice gives $A$, as one can see in Eq. (A22). The index $i$ in the abscissa runs over the first 50 $\Pi$ and $\Sigma$ states that contribute to the Coriolis mixing of the initial and final levels in the transition.](image-url)
nearly linear in the $P$ and $Q$ operators of the stretches. In summary, we observe that systematic cancellation of lower and upper state contributions to the first order HW coefficient is a general feature, which makes the HW effect quite sensitive to the PES and DMS surfaces. This effect is counter to our initial expectations that we physically expect that the Coriolis effect on the high energy, large amplitude upper state would be much more important than on the ground zero point level.

IV. COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

In Table I we report the calculated HW $A$ and $f$ factors for all perpendicular transitions that could be compared with available experimental data. Besides the large disagreement for the higher overtones, another major point to be noticed is that the experimental values by Maki et al.\textsuperscript{12,13} show a much larger variation with isotopic substitution than the calculated ones ($01^10\rightarrow000$ and $01^11\rightarrow000$ transitions). In fact, this is also in contrast to our two experimental values for the $11^15\rightarrow000$ transition in HCN and $\text{H}^{13}\text{CN}$, which are very close. This disagreement could result from our neglect of the isotopic effect on the DMS, due to a rotation of the Eckart axes. While we did not check the consequences of this effect on our calculations, it seems unlikely that this effect could give rise to such a large isotopic variation of the HW coefficients. Therefore, at this moment we do not have a plausible explanation for the large isotopic variation of the HW coefficients observed by Maki et al.

We expect the first-order perturbation treatment to be an excellent approximation. Thus, in order to rationalize the poor agreement between our theoretical estimates and the observed value of the HW coefficients, we will consider our approximate treatment of the bending dynamics and possible inadequacy of the PES and DMS.

The harmonic approximation should describe the bending motion accurately because the states important to our calculations involve only 0 or 1 bending quanta. In addition, stretch–bend interaction is quite elusive in HCN: almost no perturbations are found, even in the higher stretching overtones, and two-dimensional \textit{ab initio} calculations of this molecule perform unusually well. This is probably the combined effect of a small stretch–bend anharmonic coupling and of effective frequencies whose ratios are not favorable to the occurrence of quasi-resonances. The lowest order near resonances are that twice the CN harmonic frequency is almost 6 times that of the bending, while twice the CH frequency is somewhat smaller than 10 times the bend (the HCN harmonic wave numbers are 2127, 727, and 3440 cm$^{-1}$). In addition, the effect of anharmonicity is to tune the effective stretching frequencies away from these near resonances when the stretches are excited as in the observed overtone transitions. Notice that symmetry allows only anharmonic resonances with even number of quanta in the bending mode.

In the region of interest, the excellent fit of the observed frequencies by the CMH PES seems a good indication of its accuracy. Therefore by exclusion, the DMS is the least certain component of the present calculation. It has been shown\textsuperscript{25} that the overtone intensities from the ground state are especially sensitive to the repulsive part of the PES. The fact that the CCSD(T) DMS predicts accurate overtone intensities likely indicates that this surface is reliable in the region of the repulsive wall, but it cannot assure a global accuracy. On the other hand, the HW effect appears to be more sensitive to global features of the DMS. In fact, we have shown that it is given by the mixing of several zero-order transition moments, some of which connect overtone wave functions that are relatively close in energy. There is no reason to think that the dipole matrix element between two such wave functions should be particularly sensitive to the repulsive wall region of the PES. It should be noted that the predicted perpendicular band intensities are in significantly worse agreement with experiment than are those of the parallel bands. This suggests that the perpendicular, $\mu_z$, dipole moment surface is less accurate than the parallel, $\mu_x$, surface, at least as long as the molecule remains linear. Given the obvious loss of symmetry when the molecule bends, this is perhaps not an unexpected result.

To examine how different features of the DMS influence the predictions, we determined numerically the sensitivity of the HW $A$ coefficient and of the transition moment to variation of the coefficients of the DMS polynomial surface, which are given in Table III. In Table IV we list the dimensionless partial logarithmic derivatives of transition dipole moment and HW $A$ coefficient for the $11^15\rightarrow000$ transition, taken with respect to the coefficients of the polynomial surface fit to the \textit{ab initio} CCSD(T) dipole moment points by Botschwina et al.\textsuperscript{27} Only the derivatives with magnitude larger than 0.1 are reported. Our definition of logarithmic derivative is $\partial \ln f(x)/\partial \ln x = (xf(x)/\partial x)\partial f(x)/(\partial x)$, whose meaning is quite simple. For example, $\partial \ln A/\partial \ln C(0,0,0) = 0.57$ implies that

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\partial \ln A/\partial \ln C(0,0,0)$</th>
<th>$\partial \ln A/\partial \ln C(0,0,0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(0,0,0)$</td>
<td>0.57</td>
<td>0.00</td>
</tr>
<tr>
<td>$C(1,0,0)$</td>
<td>0.46</td>
<td>0.00</td>
</tr>
<tr>
<td>$C(3,0,0)$</td>
<td>-0.40</td>
<td>0.00</td>
</tr>
<tr>
<td>$C(4,0,0)$</td>
<td>0.42</td>
<td>0.00</td>
</tr>
<tr>
<td>$C(1,0,1)$</td>
<td>1.94</td>
<td>-1.55</td>
</tr>
<tr>
<td>$C(2,0,1)$</td>
<td>-0.58</td>
<td>0.46</td>
</tr>
<tr>
<td>$C(3,0,1)$</td>
<td>-2.80</td>
<td>2.23</td>
</tr>
<tr>
<td>$C(4,0,1)$</td>
<td>0.40</td>
<td>-0.31</td>
</tr>
<tr>
<td>$C(0,1,1)$</td>
<td>-0.19</td>
<td>0.16</td>
</tr>
</tbody>
</table>

\[\alpha\text{CH} \quad 5.56 \quad -2.97\]

\[\alpha\text{CN} \quad -1.47 \quad 0.96\]

\[V(2,0) \quad -0.21 \quad -1.64\]

\[V(0,2) \quad -0.80 \quad 0.46\]

\[V(4,0) \quad 0.58 \quad -0.26\]

\[V(6,0) \quad 0.25 \quad -0.11\]
a variation of 1% in the $C(0,0,0)$ will produce a variation of 0.57% in the HW $A$ coefficient of the $1^1S^5 ← 000$ transition. To obtain these derivatives, we iterated the calculation of the intensities and the HW coefficients after systematic “small” relative variation of each of the DMS coefficients. To check against problems of numerical stability, the whole procedure was repeated with the relative variations equal to 0.1%, $10^{-4}$, and $10^{-5}$. The values of the derivatives where found to be independent of the variation size, except for a few which dropped to zero in the $10^{-5}$ case, due to numerical roundoff.

The DMS sensitivity pattern displayed in Table III is consistent with the HW effect as described before in terms of Coriolis mixing of $\Sigma$ and $\Pi$ states and interference of the induced transition matrix elements. In fact, the $A$ coefficient are sensitive to both the $C(m,n,0)$ and $C(m,n,1)$ coefficients, while the intensities are dependent only on the $C(m,n,0)$ coefficients. Note that in parallel transitions the intensities would depend only on the $C(m,n,0)$. With respect to the values themselves, it is evident that the sensitivity of $A$ and of the transition moment to the $C(m,n,1)$ coefficients are very well correlated by a factor of about $-1.26$. Another evident feature, which follows from the large dipole component of the CH bond, is that the CH stretch DMS coefficients are very well correlated by a factor of about $-1.26$. These sensitivity patterns are generally valid for the transitions we are considering, therefore the values given in the table for a specific transition are typical for other perpendicular bands too. This suggests that inaccuracies in the DMS might be not sufficiently well defined as for the DMS. Somewhat unexpectedly, the HW parameter depends upon both the parallel and the perpendicular components of the DMS, while the intensities depend only on one or the other, depending on the type of transition. This indicates that the good performance of the DMS in predicting the intensities is not incompatible with a poor prediction of the HW effect. In particular, this might indicate that the perpendicular DMS component is less accurate than the parallel component, as it is also indicated by the reduced accuracy of the perpendicular band intensities. We have also observed that the order of the DMS polynomial expansion seems not to be sufficiently converged with respect to the intensities and the HW coefficients. This suggests that the problem is with the polynomial expansion and not with the ab initio DMS points it was fit to.

With respect to the analysis of the sensitivity to the PES expansion parameters, it similarly shows that the HW effect and the transition intensities are sensitive to different aspects of the potential. However, the PES expansion is subjected to the stringent requirement of accurately reproducing the vast data set of HCN band origins and rotational constants. But, because of the extremely small size of overtone transition moments, very small changes in the vibrational wave func-

V. CONCLUSION

At the origin of this work, is the sizable HW distortion of the $R/IP$ branch intensities affecting the few perpendicular transitions we observed in the linear molecule HCN. We have used perturbation theory to predict the effect of ro-vibrational interactions on the overtone intensities, and in the Appendix we give explicit expressions for the HW parameters in terms of transition dipole moments among zero-order vibrational wave functions. As it turns out, the treatment is rather more complex than in the case of fundamental vibrational transitions, and numerical evaluation of these expressions is required. Calculations have been performed using an approximate variational basis that results from the diagonalization of the best empirical PES today available for HCN, and a polynomial fit to ab initio CCSD(T) DMS points, which reproduces rather accurately all the known overtone intensities.

As this model completely fails to give the correct size of the HW effect, we have argued that either the PES or the DMS might be not sufficiently accurate. We have calculated the sensitivity of the HW parameters and of the band intensities to the DMS coefficients. We have found the physically simple result that the HW parameter depends upon both the parallel and the perpendicular components of the DMS, while the intensities depend only on one or the other, depending on the type of transition. This indicates that the good performance of the DMS in predicting the intensities is not incompatible with a poor prediction of the HW effect. In particular, this might indicate that the perpendicular DMS component is less accurate than the parallel component, as it is also indicated by the reduced accuracy of the perpendicular band intensities. We have also observed that the order of the DMS polynomial expansion seems not to be sufficiently converged with respect to the intensities and the HW coefficients. This suggests that the problem is with the polynomial expansion and not with the ab initio DMS points it was fit to.
tions, which would have minor effects on the vibrational energy levels, could have a large effect on the intensities.\textsuperscript{25}

We conclude that the HW effect can be a valuable probe of the accuracy of the DMS of PES available for a given molecule. Given the progress in high sensitivity and high resolution techniques, this effect is likely observable in several systems, especially in perpendicular overtone transitions. Too often in the past, the possibility of HW perturbations of the intensity profile has been neglected. Besides the loss of valuable information, this can lead to errors in the evaluation of vibrational intensities. In the present case of HCN, more investigations, both experimental and computational, are needed to shed more light over this problem, which remains partially unresolved.

ACKNOWLEDGMENTS

We wish to thank Professor W. Quapp and Dr. A. Maki for sharing with us their data prior to publication and Professor P. Botschwina for providing a copy of P. Sebald’s thesis and his CCSD(T) dipole results prior to publication. Dr. J. K. G. Watson is acknowledged for a careful reading of a draft version of this paper. This work was supported by a grant from the National Science Foundation.

APPENDIX A: RO-VIBRATIONAL PERTURBATION EXPANSION OF THE TRANSITION STRENGTH IN A TRIATOMIC LINEAR MOLECULE

In this Appendix we derive a general expression for the $J$-dependent ro-vibrational transition intensity from $\Sigma(v_{\text{bend}}=0)$ to $\Pi(v_{\text{bend}}=1,/=1)$ overtone states of a linear triatomic molecule. This expression is good to the first perturbative order in the rotation–vibration coupling, with the zero order given by the separable Hamiltonian of vibrations and rigid rotations. We derive the simple form $\text{HL}(m)fS_0(1+Am)^2$, where $m=J+1$ in the $R$ branch and $m=-J$ in the $P$ branch. $\text{HL}(m)$ is the Hönig–London rotational coefficient, $A$ is the HW coefficient and $f$ gives a correction to $S_0$, which is the zero-order vibrational intensity of the $\Pi-\Sigma$ transition. For the $Q$ branch line intensities we obtain $\text{HL}_Q(J)fS_0(1+A_Q(J+1))^2$.

In the following framework, it is relatively easy to derive corresponding expressions for transitions other than $\Pi-\Sigma$, including second-order perturbation corrections, which describe the $\Pi-\Sigma$ HW effect to powers higher than $J^2$. In our case, the experimental error bars allow to determine only a linear $J$ dependence. We will show that higher perturbative corrections to the coefficients of $J$ and $J^2 (2A$ and $A^2)$ are quite negligible in $\Pi-\Sigma$ transitions. Two important points should be underlined from the beginning. The first is that even very small state mixing, well described by first-order perturbation theory, can produce a sizable HW effect, due to the strong transition moment carried by some of the mixed components. The second point, which can be source of confusion, is that the correspondence between perturbative orders and powers of $J$ is not trivial.

The ro-vibrational Hamiltonian of a linear molecule in the Born–Oppenheimer approximation was rigorously derived by Watson\textsuperscript{26} only in 1970:

$$H = \sum_{k} \frac{P_k^2}{2} + \frac{1}{2I(Q)} \{(J_x - \pi_x)^2 + (J_y - \pi_y)^2\} + V(Q),$$

(A1)

where $Q_k$ and $P_k$ are the normal-coordinates position and momentum operators, $I(Q)$ is the effective moment of inertia, $J$ is the total angular momentum, $\pi$ is the vibrational angular momentum associated with the twofold degenerate bending motion, and $V(Q)$ is the nuclear PES. The $z$ axis of the molecule-fixed Cartesian coordinates is along the $C_{\infty}$ symmetry axis, while $x$ can be assigned to the molecule rotation axis, so that the projection of $J$ along $y$ is zero. The space-fixed Cartesian axes will be labeled by $X,Y,Z$. Greek indices will be reserved for $x,y,z$.

The vibrational angular momentum is defined by

$$\pi_{\alpha} = \sum_{k,l} b_{kl}^\alpha Q_k P_l$$

with

$$b_{kl}^\alpha = \sum_{\beta,\gamma} \epsilon_{\alpha\beta\gamma} \sum_{i} \ell_{\beta,\gamma,i} r_{\alpha,i},$$

(A2)

where the coefficient $\epsilon_{\alpha\beta\gamma}$ gives the component of the mass-weighted Cartesian displacement $\rho_{\alpha i} = \sqrt{m_i} r_{\alpha i}$ of the atom $i$ for the normal coordinate $Q_k$; $\rho_{\alpha i} = \sum_{\beta,\gamma} \ell_{\beta,\gamma,i} Q_k$. The symmetry of the normal modes allows to decide immediately which of the Coriolis $\zeta_{\beta,\gamma}^\alpha$ coefficients must be zero. For the nonzero coefficients in HCN and its isotopomers, the following values were calculated using the force constants by Carter, Mills, and Handy\textsuperscript{6}:

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>$\zeta_a = \zeta_{14}^a = -\zeta_{13}^a$</th>
<th>$\zeta_b = \zeta_{24}^b = -\zeta_{23}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>0.154 13</td>
<td>0.988 05</td>
</tr>
<tr>
<td>H13CN</td>
<td>0.164 35</td>
<td>0.986 40</td>
</tr>
<tr>
<td>HC15N</td>
<td>0.154 81</td>
<td>0.987 94</td>
</tr>
</tbody>
</table>

(A3)

Here, the normal mode numbering is: $1 = \text{CN}, 2 = \text{CH}, 3 = x$ bend, $4 = y$ bend. This labeling is not standard and will be used only in this Appendix. The signs of the Coriolis coefficients depends on the choice of the coordinate systems for the displacements. Here, the $z$ axis points from the $C$ to the $N$ atom, and the signs of the $z$ displacements of all 3 atoms are relative to the direction of the $z$ axis. Notice that in HCN the stretching normal modes can be easily identified and labeled by the bond mode with predominant amplitude.

The Coriolis and centrifugal-distortion terms ($H_c$ and $H_d$) coupling rotations and vibrations will be treated as perturbations to the linear-molecule rigid-rotor Hamiltonian $H_0$. They are obtained by expanding the middle term of the full Hamiltonian given above, subtracting the rigid-rotor term containing the equilibrium moment of inertia $I_0$, and neglecting $-(\pi_x^2 + \pi_y^2)/2I$, which corresponds to a rotation-independent frequency shift:
\[ H_c = -\frac{1}{I(Q)} (J_x \pi_x + J_y \pi_y) \]
\[ = -\frac{1}{2I(Q)} (J_x \pi_- + J_y \pi_+), \quad (A4) \]
\[ H_d = \frac{1}{2} \left( \frac{1}{I(Q)} - \frac{1}{I_0} \right) (J_x^2 + J_y^2) = \frac{1}{2} \left( \frac{1}{I(Q)} - \frac{1}{I_0} \right) (J^2 - J_z^2). \quad (A5) \]

Notice that the \( \pi_a \) satisfy the usual commutation rules for the angular momentum so that \( \pi_\pm = (\pi_x \pm i \pi_y)/2 \) behave as raising/lowering operators for \( \pi_x \). On the other hand, the \( J_\alpha \) have anomalous commutation \( [J_\alpha, J_\beta] = -iJ_\gamma \) with cyclic values of \( \alpha, \beta, \) and \( \gamma \). We will adopt the convention of defining \( J_\pm = (J_\times \pm iJ_\gamma)/2 \), which behave as lowering/raising (notice the inversion) operators for \( J_z \). This subtle anomaly depends on the fact that the total angular momentum \( J \) is defined as the generator of rotations in the space-fixed frame, where it obeys normal commutation rules. The anomalous rules are a consequence of transforming the operator to the rotating body-fixed frame (Ref. 8 p. 84).

The ro-vibrational wave functions that diagonalize \( H_0 \) are formed by the products of each symmetric-top rotational eigenfunction \( |JM\rangle, \text{with } M \text{ and } K \text{ quantum numbers of the } J \text{ projections along } Z \text{ and } z \) with the vibrational eigenfunctions having the same value of \( K \) as an eigenvalue of \( \pi_z \). This ensures that the Szavetz condition is satisfied. As an example, the zero-order wave functions for the overtone state 01^1(6) (standard notation), are
\[ |01^1\rangle = \frac{1}{\sqrt{2}} (|0610\rangle \pm i|0601\rangle), \quad (A6) \]
where we have used the circularly polarized bending states \( |1^\pm\rangle = (|10\rangle \pm i|01\rangle)/\sqrt{2} \). By definition, \( |10\rangle \) and \( |01\rangle \) are the bending states linearly polarized along \( x \) and \( y \).

One of the effects of the Coriolis coupling \( H_c \) is to remove the degeneracy in \( K \). It has been shown\(^{25}\) that the "\( \pi \)" linear combinations of the II states with \( K = \pm 1 \) partially diagonalize \( H_c \); with respect to the previous example, we are here referring to the II states \( |0\rangle_1^+|JM\rangle + \pm |0\rangle_1^-|JM\rangle \). Since the parity of the "\( \pi \)" combinations is \(-1\), these states can be mixed by \( H_c \) (which commutes with parity) with \( \Sigma \) and \( \Sigma_2 \) \( \Delta\nu_{\text{vib}} = 2 \\ell = 2 \) states of the same \( J \), while the "\( \pi \)" combinations do not mix at all (first order). On the other hand, since the transition dipole moment \( \mu \) changes the parity, the "\( \pi \)" combinations participate only to \( P \) and \( R \) branch transitions to \( \Sigma \) and \( \Sigma_2 \) states, while the "\( \pi \)" combinations participate to the \( Q \) branch. In a perpendicular \( \Pi - \Sigma \) transition, the Coriolis mixing of a small amount of \( \Sigma \) character to the II state carries with it a much larger parallel \( \Sigma_2 \mu |\Sigma_2 \rangle \) transition moment, and determines the observed HW anomaly of R/P-branch \( J \)-dependent intensities. Similarly, the mixing of some II character to the \( \Sigma \) state also gives a contribution to this effect, through a sizable \( \Sigma_2 \mu |\Pi \rangle \) transition moment. Mixing with \( \Sigma_2 \) states has a negligible effect, since the transition moment for a change of \( \Delta\nu_{\text{vib}} = 2 \) is small.

\[ \Delta(\nu_{\text{vib}} = 2\ell = 2) \text{ states also mix to the II states, but the } \Delta - \Sigma \text{ transition moment is zero (} \Delta\ell = 0 \). The accepted convention\(^{28}\) is to label as "\( \pi \)" the states with parity \(-1\)^\((l)\), and as "\( \ell \)" the others. In our case, the generic \( \Pi_{\ell j} \) states are defined as
\[ |\Pi_{\ell j}JM\rangle = \frac{1}{\sqrt{2}} (|\Pi_{\ell j}JM1 \rangle \pm |\Pi_{\ell j}JM - 1 \rangle). \quad (A7) \]

At a first glance, the intensity \( J \) dependence of a \( \Pi - \Sigma \) overtone transition would appear to be dominated by mixing of the \( \pi \) sublevels with the closest \( \Sigma \) states only. On the contrary, all the \( \Sigma \) states with energy comprised between the II and \( \Sigma \) state give a relevant contribution. The mixing coefficients are proportional to \( \langle \Pi_{\ell j}|H_c|\Sigma \rangle/(E_{\Sigma} - E_{\Pi}) \), while the contribution of each \( \Sigma \) state to the transition moment is proportional to \( \langle \Sigma |\mu|\Sigma \rangle \). In a harmonic approximation of the vibrational potential \( V(Q) \), the \( \mu \) matrix elements would be zero for changes of more than one vibrational quanta, but due to the substantial anharmonicity of the CH chromophore, the \( \langle \Sigma |\mu|\Sigma \rangle \) matrix element decreases almost exponentially with the \( \Sigma - \Sigma \) difference in vibrational quanta. On the other hand, \( \mu \) and \( H_c \) are both nearly linearly dependent on the \( Q \)’s; the decrease of one matrix element is thus almost exactly compensated by the increase of the other, for all \( \Sigma \) states between the initial \( \Sigma \) and the final II state. The remaining slow \( 1/\Delta E \) dependence will give a larger weight to the \( \Sigma \) states closer to the II state, but will not completely eliminate the contribution of the more distant \( \Sigma \) states. A similar argument holds for \( \Pi \) states mixing with the \( \Sigma \) state.

While \( H_c \) is nearly linear in the bending momentum and position operators, \( H_d \) does not depend on these operators at all, which can be deduced from the definition of \( \pi_z \) in Eq. (A2) and \( I(Q) \) in Eq. (A26). As we have seen, \( H_c \) has matrix elements between states which differ by one quantum of bending excitation, while \( H_d \) must preserve the bending quantum number. Therefore, \( H_d \) mixes II with II and \( \Sigma \) with \( \Sigma \) states only and the transition moment it introduces in a \( \Pi - \Sigma \) transition is perpendicular in character, and thus is not expected to give a large contribution to the HW coefficient. However, we will include the \( H_d \) mixing terms which allowed us to confirm numerically that their effect on the intensities of the perpendicular transitions of interest is small.

We now proceed by writing the ro-vibrational wave functions to the first perturbative order,
\[ |\Sigma_{i,\ell}JM\rangle = |\Sigma_{i,\ell}0JM\rangle + \sum_i s_{ij} |\Pi_{ji}JM\rangle + \sum_i c_{ij} |\Sigma_{i,\ell'}JM\rangle, \]
\[ |\Pi_{i,\ell}JM\rangle = |\Pi_{i,\ell}0JM\rangle + \sum_{\ell'} p_{i,\ell} |\Sigma_{i,\ell'}JM\rangle \]
\[ + \sum_{\ell''} d_{i,\ell} |\Pi_{i,\ell}JM\rangle, \quad (A8) \]
where the mixing coefficients are given by
\[ s_{ij} = \langle \Pi_{i,\ell}JM\rangle |H_c| \Sigma_{i,\ell'}JM\rangle |(E_{\Sigma_{i,\ell}} - E_{\Pi_{i,\ell}})|. \]
second-order terms like \( \langle \Pi_i J' M' | H | \Pi_i J M \rangle \) \( (9) \)

\[
p_{ik} = \langle \Pi_i J' M' | H | \Pi_i J M \rangle / \langle \Pi_i J' | \Pi_i J M \rangle - \langle \Sigma_i J | \Sigma_i J \rangle,
\]

\[
d_{ik} = \langle \Pi_i J' M' | H | \Pi_i J M \rangle / \langle \Pi_i J' | \Pi_i J M \rangle - \langle \Sigma_i J | \Sigma_i J \rangle.
\]

Notice that the rotational dependence of the energy can be neglected. Apart from proportionality factors, the transition intensity is (Ref. 8, p. 284):

\[
S_{J',J}(\Pi_i J' \leftrightarrow \Sigma_i J) = \sum_{M,M'} |\langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle|^2.
\]

(A10)

For simplicity we dropped the perturbative-order superscripts. The factor 3 has been introduced by assuming spatial isotropy and summing over the space-fixed components of \( \mu \).

If we substitute Eq. (A8) into Eq. (A10) and neglect second-order terms like \( \Sigma_i, \Sigma_j, p_{ik} \), etc., we see that we need 3 kinds of \( \mu_\Sigma \) matrix element:

\[
S_{J',J}(\Pi_i J' \leftrightarrow \Sigma_i J) = \sum_{M,M'} |\langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle|^2.
\]

(A11)

To simplify these matrix elements, we transform \( \mu_\Sigma \) to the rotating frame,

\[
\mu_\Sigma = \sum_{q = \pm 1.0} D_{q0}^{i_\Sigma}(\phi, \theta, \chi) \mu(1, q),
\]

where the tensorial components of \( \mu \) are \( \mu(1, \pm 1) = \mp (\mu_\Sigma \pm i \mu_\alpha) / \sqrt{2} \) and \( \mu(1, 0) = \mu_\Sigma \), and the \( D_{q0}^{i_\Sigma}(\phi, \theta, \chi) \) are the rotation matrices, which are function of the Euler angles (Ref. 8, pp. 178 and 85). Then, we need Eq. (A7), plus the definition of the symmetric top eigenfunctions (Ref. 8, p. 105)

\[
|JM Ki = \sqrt{\frac{J+1}{8 \pi}} D_{M K_1}^{i_\Sigma}(\phi, \theta, \chi)
\]

\[
= (-1)^{M-K} \sqrt{\frac{J+1}{8 \pi}} D_{M-K}^{i_\Sigma}(\phi, \theta, \chi), \quad (A13)
\]

and the following integral (Ref. 8, p. 103)

\[
\int D_{M K_1}^{i_\Sigma} D_{M K_2}^{i_\Sigma} D_{M K_3}^{i_\Sigma} d\Omega = 8 \pi^2 \left( \begin{array}{ccc} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{array} \right) \left( \begin{array}{ccc} K_1 & K_2 & K_3 \end{array} \right), \quad (A14)
\]

By also using the cyclic properties of the 3-\( J \) symbols, and their explicit expressions from Zare’s book (Ref. 8, Table 2.5), the required matrix elements for the \( R \) and \( P \) branch \( (J' = J \pm 1) \) simplify to

\[
\langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle = F(J', J, M', M) \times \langle \Pi_i J | \mu_\Sigma | \Sigma_i J \rangle \sqrt{|m+1|},
\]

\[
\langle \Pi_i J' M' | \mu_\Sigma | \Pi_i J M \rangle
\]

\[
= -F(J', J, M', M) \langle \Pi_i J | \mu_\Sigma | \Pi_i J M \rangle sgn(m) \times \sqrt{|m-1| - (m+1)|m|}.
\]

(A15)

\[
\langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle = -F(J', J, M', M) \times \langle \Sigma_i J | \mu_\Sigma | \Sigma_i J \rangle sgn(m) \sqrt{|m|},
\]

\[
F(J', J, M', M) = (-1)^{J'+M} \left( \begin{array}{ccc} J' & 1 \\ M'-M \end{array} \right),
\]

where we have used the linearly-polarized bending states \( |\Pi_i J' M' \rangle = |n_1 n_2 1 0 \rangle \), which are more convenient for direct numerical evaluation. We also list the other nonzero matrix elements among \( \Sigma \) and \( \Pi \) states, which are needed to carry out the calculations for the \( Q \) branches or (partly) for the second order:

\[
\langle \Sigma_i J' M' | \mu_\Sigma | \Pi_i J M \rangle = -F(J', J, M', M) \times \langle \Sigma_i J | \mu_\Sigma | \Pi_i J M \rangle \sqrt{|m+1|},
\]

\[
\langle \Pi_i J' M' | \mu_\Sigma | \Pi_i J M \rangle = -F(J', J, M', M) \times \langle \Pi_i J | \mu_\Sigma | \Pi_i J M \rangle \sqrt{|m+1|}.
\]

(A15a)

\[
\langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle = \langle \Pi_i J' M' | \mu_\Sigma | \Sigma_i J M \rangle = F(J', J, M', M) \times \langle \Sigma_i J | \mu_\Sigma | \Pi_i J M \rangle \sqrt{|2J+1|}.
\]

(A16)

Notice that for the second-order perturbation, matrix elements involving states with \( \nu_{\text{bend}} = 2 \) are also needed, and can be calculated following the same procedure.

With respect to the \( H_c \) mixing coefficients, their \( J \) dependence can be made explicit by decomposing \( H_c \) into the product of the operators

\[
U = \frac{1}{2I(Q_1, Q_2)} \quad \text{and} \quad K = -(J_+ \pi_+ - J_- \pi_+).
\]

(A17)

These operators are real and Hermitian (therefore symmetric), and they commute: \( H_c = UK = KU \). In addition, \( U \) is diagonal in the rotational and bending degrees of freedom. Therefore,
\[ s_{ij} = \frac{\langle E(\Sigma_j) - E(\Pi_i) \rangle^{-1}}{\sum_h} \langle \Pi_i J M e | K | \Sigma_h J M \rangle \times \langle \Sigma_h J M | U | \Sigma_j J M \rangle \]

\[ = \frac{\hbar \sqrt{J(J+1)} \sum_h \langle \Pi_i^J | K | \Sigma_h \rangle \langle \Sigma_h | U | \Sigma_j \rangle}{E(\Sigma_j) - E(\Pi_i)} \]

\[ = \sqrt{m(m-1)} \tilde{s}_{ij}, \quad (A18) \]

\[ p_{ik} = \frac{\hbar \sqrt{J(J'+1)} \sum_h \langle \Sigma_i | U | \Sigma_h \rangle \langle \Sigma_h | K | \Pi_i^J \rangle}{E(\Pi_i) - E(\Sigma_j)} \]

\[ = \sqrt{m(m+1)} \tilde{p}_{ik}, \]

\[ \tilde{p}_{ik} = -\tilde{s}_{ki}. \]

Here, we have extracted the \( \sqrt{J(J+1)} \) factors from the \( K \) matrix elements using Eq. (A7) and Eq. (3.49) in Zare\(^8\) for the anomalous \( J \pm \) matrix elements. Then we have used the definition of \( m \) for \( j' - j, R/P \) branch transitions. We have therefore written \(|K|\), ‘reduced’ matrix elements which will be given explicitly in Eq. (A27), and we have introduced the \( J \)-independent coefficients \( \tilde{s}_{ij} \) and \( \tilde{p}_{ik} \).

\[ S_n(\Pi_k \rightarrow \Sigma_j) = [m+1] \left[ \langle \Pi_k^J | \mu_s | \Sigma_j \rangle - (m-1) \sum_i \tilde{s}_{ij} \langle \Pi_i^J | \mu_s | \Pi_k^J \rangle - m \sum_j \tilde{p}_{ik} \langle \Sigma_j | \mu_s | \Sigma_j \rangle \right] + [m(m+1) - 1] \sum_{i \neq j} \tilde{d}_{ik} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle \]

\[ + m(m-1) \sum_k \tilde{d}_{ik} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle \]

\[ = \text{HL}_{\Pi \Sigma} (m) f S_0 (1 + Am)^2 , \quad (A21) \]

where we have neglected higher powers of \( m \). \( \text{HL}_{\Pi \Sigma} (m) = [m+1] \) is the normal H"{o}nl–London factor for the \( R/P \) branch of \( \Pi \rightarrow \Sigma \) transitions in absence of ro-vibrational coupling, and the other quantities are defined as

\[ S_0 = \langle \Pi_k^J | \mu_s | \Sigma_j \rangle^2 , \]

\[ f = \sqrt{1 + \langle \Pi_k^J | \mu_s | \Sigma_j \rangle - (m-1) \sum_i \tilde{s}_{ij} \langle \Pi_i^J | \mu_s | \Pi_k^J \rangle - m \sum_j \tilde{p}_{ik} \langle \Sigma_j | \mu_s | \Sigma_j \rangle} , \quad (A22) \]

\[ A = \frac{1}{f^2 \langle \Pi_k^J | \mu_s | \Sigma_j \rangle} \left[ \sum_i \left( \tilde{s}_{ij} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle - \langle \Pi_i^J | \mu_s | \Pi_k^J \rangle \right) - \sum_{i \neq j} \tilde{c}_{ij} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle + \sum_{i \neq k} \tilde{d}_{ik} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle \right] , \]

so that \( A \) is the conventional HW coefficient and \( S_0 \) is the unperturbed vibrational intensity. Notice that the presence of the \( f \) factor shows that the HW effect does not go to zero for \( m = 0 \).

The same steps lead to an analogous expression for the \( Q \) branch intensities:

\[ S_Q^n(\Pi_k \rightarrow \Sigma_j) = \text{HL}_{\Pi \Sigma}^Q (J) f S_0 (1 + A_Q J(J+1))^2 , \quad (A23) \]

where \( \text{HL}_{\Pi \Sigma}^Q (m) = 2J+1 \) is the H"{o}nl–London factor for the \( Q \) branch of \( \Pi \rightarrow \Sigma \) transitions. While the \( f \) factor happens to be exactly the same as for the \( P \) and \( R \) branches, the \( A_Q \) coefficient depends only on the centrifugal mixing:

\[ A_Q = \frac{1}{f^2 \langle \Pi_k^J | \mu_s | \Sigma_j \rangle} \left[ \sum_{i \neq j} \tilde{c}_{ij} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle + \sum_{i \neq k} \tilde{d}_{ik} \langle \Pi_i^J | \mu_s | \Sigma_j \rangle \right] . \quad (A24) \]

We have still to express explicitly the \( K \) and \( U \) matrices entering in the mixing coefficients, which were defined in Eq. (A18) and Eq. (A19):

\[ \tilde{s}_{ij} = \hbar \langle E(\Sigma_j) - E(\Pi_i) \rangle^{-1} \sum_h \langle \Pi_i^J | K | \Sigma_h \rangle \langle \Sigma_h | U | \Sigma_j \rangle , \quad (A25) \]
explicit expressions of the vibrational angular momentum since they have values on the order of the square of those for $I$ where

$$c_{ij} = \frac{\hbar^2 (\Sigma_i | U | \Sigma_j)}{E(\Sigma_j) - E(\Sigma_i)}, \quad d_{ij} = \frac{\hbar^2 (\Pi_i | U | \Pi_j)}{E(\Pi_j) - E(\Pi_i)}.$$  

To calculate matrix elements of $U$, we can use

$$1 = \frac{I_0}{I(Q_1, Q_2)} = \left( I_0 + \sum_k a_k Q_k^2 \right)^{-1},$$

with

$$a_k = 2 \sum l^n r_{ci}^0 Q_{ci}^k,$$

(A26)

where $I_0$ is the equilibrium moment of inertia and $r_{ci}^0$ are the $z$ components of the equilibrium atomic positions with respect to the center of mass. Since the moment of inertia depends only on the stretching coordinates $Q_1$ and $Q_2$, its matrix can be easily evaluated in a variational eigenfunction basis for the stretching coordinates problem by using the normal mode $L$ matrix to transform between $Q_1, Q_2$ and $\Delta r_{CH}, \Delta r_{CN}$. The inversion of $(I_0 + \frac{1}{2} \sum_k a_k Q_k^2)$ is then a simple numerical matrix operation.

With respect to the matrix elements of $K$, we use the explicit expressions of the vibrational angular momentum $\pi_z$ given before in terms of $\pi_{x,y}$, which are defined in Eq. (A2). We obtain

$$\langle \Pi_i | K | \Sigma_h \rangle$$

$$= \langle n_1^i n_2^i | 1^s | K | n_1^h n_2^h \rangle$$

$$= 2i \left( \langle 1^s | P_3 | 0 \rangle \left( \xi_0 (n_1^i n_2^i | Q_1 | n_1^h n_2^h) + \xi_0 (n_1^i n_2^i | Q_2 | n_1^h n_2^h) \right) - \langle 1^s | Q_3 | 0 \rangle \right)$$

$$\times \left( \xi_0 (n_1^i n_2^i | P_1 | n_1^h n_2^h) + \xi_0 (n_1^i n_2^i | P_2 | n_1^h n_2^h) \right).$$

(A27)

The bending position and momentum matrix elements $(Q_1$ and $P_3$) involve only the first two bending levels and with good approximation the bend can be considered a separable degree of freedom and calculated in the harmonic approximation. The rest of the expression contains matrix elements that can be obtained directly in the variational basis for the stretches-only problem.

As we anticipated, the Coriolis coupling mixing is associated with strong parallel transition matrix elements, while the centrifugal coupling is multiplied by much smaller perpendicular transition matrix elements. The numerical values for the mixing coefficients and the transition elements are discussed in the main body of the paper.

With respect to the contribution of the different perturbative orders to a given order in the HW expansion (not counting the Hön–London factor $J$ dependence), we see that in general the $n$th perturbative terms in $H_c$ may contribute to all powers of $J$ less than $J^{2n}$, while $H_d$ may contribute to all those less than $J^{4n}$. With respect to the relative importance of centrifugal and Coriolis interaction, one finds that the mixing coefficients associated with $H_d$ are much smaller, since they have values on the order of the square of those for $H_c$. In addition, one has to consider the relative size of the mixing contributions to the zero-order transition moment. The scenario depends on the character of the transition. For perpendicular bands, we have seen that $H_c$ mixing contributes parallel type transition moment, while $H_d$ perpendicular type. Since in HCN, parallel overtone transition moments are an order of magnitude or more larger than the corresponding perpendicular ones, this goes in the same direction as the relative size of the mixing coefficients, making centrifugal effects even more negligible. The scenario is reversed in parallel transition, which gives a compensation effect that makes the centrifugal mixing no more so clearly negligible. The situation complicates further if one considers that the second order mixing coefficients by $H_c$ have the same size as those first order in $H_d$ and are also associated to parallel transition moments. Therefore, it appears that to estimate correctly the HW effect in parallel overtone transition, one should include the contribution of the first order in $H_d$ and the second in $H_c$. Finally, we note that the fact that parallel transition moments dominate over the perpendicular ones has the consequence that the HW effect is much smaller and difficult to observe in parallel bands.

13. W. Quupp (private communication).
23. P. Botschwina (private communication).