The \( \nu_1 \) vibrational predissociation lifetime of (HCN)\(_2\) determined from upperstate microwave-infrared double-resonance measurements

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We have successfully applied upper state microwave-infrared double-resonance spectroscopy, with optothermal molecular beam detection, to the determination of the (HCN)\(_2\) vibrational predissociation lifetime upon excitation of the outside CH stretching mode (\( \nu_1 \)). The measured lifetime is 1.7(5) \( \mu \)s. At this time this is the longest lifetime for a hydrogen bonded complex determined with such precision. We have also been able to accurately measure several upper state transition frequencies, therewith revealing the presence of a perturbation in the spectrum that shifts at least one of the rotational levels by an amount on the order of 1 MHz, and appears to decrease the lifetime of the level measurably. A rate equation approach predicts that this experiment will have a negligible signal to noise ratio for upper state lifetimes much shorter than the infrared (IR) laser–molecular beam interaction time, such as is the case here. In order to explain the presence of a double resonance signal, we have proposed a new mechanism that is based upon a coherent interaction model. The technique of microwave–IR double resonance should be widely applicable to the measurement of dissociation lifetimes in the presently difficult-to-access range from about 100 ns to 100 \( \mu \)s. This is a range in which a significant number of complexes are known to have vibrational predissociation lifetimes.

I. INTRODUCTION

The spectroscopy of weakly bound, van der Waals or hydrogen bonded, complexes is perhaps the most important source of precise information on intermolecular forces, and as such is a very active field of research. The experimental information obtained for these systems has traditionally come from rotational spectroscopy in the microwave region of the spectrum, and includes structural parameters such as rotational constants, electric quadrupole constants, dipole moments, and dissociation energies.

However, in the past 10 years, vibrational (infrared) spectroscopy has become an equally important tool in the study of weakly bound complexes. When a high-frequency vibrational mode associated with a chemical bond in the complex is excited, very often the complex becomes metastable with respect to dissociation. Because of the typically slow rate of dissociation, this generally results in a well-resolvable vibration-rotation spectrum, in which the individual rotational lines exhibit a homogeneous (Lorentzian) broadening. Thus the rate of dissociation can be deduced from the homogeneous broadening if other sources of lifetime broadening can be neglected. In general there is the possibility that the molecule will undergo intramolecular vibrational energy relaxation (IVR) before dissociation occurs and if the density of "background" (bath) states is sufficiently large this may also contribute to a Lorentzian broadening of the observed transitions. However, for nearly all weakly bound complexes studied to date by infrared (IR) spectroscopy this large molecule limit of IVR is not reached and the effects of IVR appear as local perturbations that affect at most a few rotational lines in the spectrum. Therefore, in practically every case, it becomes possible to distinguish the effects of IVR and of vibrational predissociation. Consequently, an experimentally observed Lorentzian broadening of the rovibrational lines can be confidently interpreted in terms of a vibrational predissociation lifetime.

Predissociation lifetimes have been found to provide an extremely sensitive test of state-of-the-art calculations of the dynamics, and of the potential energy surfaces used in it. This point is well illustrated by the recent calculations of the predissociation lifetime (upon HF excitation) of ortho H\(_2\)-HF carried out by Zhang et al. The calculation predicts a 1600 ns lifetime, while the experimentally determined lifetime is only 27 ns. This result is quite puzzling considering the excellent agreement between the theoretical and experimental lifetimes of ortho and para D\(_2\)-HF, since the potential energy surface used in both cases is the same. The large range spanned by the observed vibrational predissociation lifetimes for a range of rather similar complexes, as well as the mode-specificity of the dissociation process, are in themselves already strong indications of the sensitivity of the lifetime to small changes in the complex.

At the same time that state-of-the-art calculations still experience serious difficulties in delivering quantitatively correct results for even the most simple (three-atomic) systems, simple correlation laws, such as the momentum gap law, have been relatively successful in explaining the general trends. For example, the predissociation lifetime of HCN–HF has been measured, both upon fundamental excitation of the CH stretch (\( \nu_1 \)) (Ref. 10) and upon overtone excitation of the same mode (2\( \nu_1 \)), showing that the
ratio of these two measurements is in agreement with a simple model based on first-order perturbation theory.\(^{11}\)

The above considerations have motivated our study of the vibrational predissociation lifetime of the HCN dimer upon excitation of the \(v_1\) mode (the nonbonded CH stretch). This dimer can be regarded as a model system in the study of vibrational predissociation and it has been the focus of much research, yet, until now, the lifetime of the \(v_1\) mode has eluded determination. The IR spectrum recorded by Miller et al.,\(^{12}\) limited by the instrumental line-width, has provided an upper limit to the Lorentzian broadening of the lines of \(-1\) MHz, corresponding to a lower limit to the lifetime of 140 ns. At the same time, the detection technique established that the dimer dissociated with a lifetime of 0.3 ms or less. Up to date, no spectroscopic method has been used to determine vibrational predissociation lifetimes longer than \(-100\) ns, while a significant number of complexes are known to have vibrational predissociation lifetimes in this difficult-to-access range (from say 100 ns to about 100 \(\mu\)s). In the present report we show that the technique of microwave-infrared double-resonance (MW-IR-DR) can be used to determine vibrational predissociation lifetimes that cover a significant part of this range.

The technique of MW-IR-DR has established itself as an extremely useful spectroscopic tool, for providing both increased sensitivity and spectral resolution over pure IR spectroscopy. For these reasons it has been used successfully to simplify complicated infrared spectra, to observe weak transitions, to study collision induced-transitions and energy transfer processes, and to observe rotational transitions in vibrationally excited states. MW-IR-DR has been applied to the study of stable molecules in their ground and vibrationally excited states, as well as of molecular ions and free radicals. In very few cases the method has been applied to weakly bound complexes.

Making use of the wealth of microwave spectroscopic data for the ground state,\(^{13}\) microwave far-infrared double resonance has greatly facilitated the assignment of the van der Waals vibrations of ArHCl by Saykally and co-workers.\(^{14}\) Hayman et al. observed rotational transitions in the vibrational ground state of Ne \(\cdot\) OCS with their 5 \(\mu\)m diode laser, pulsed free jet spectrometer, but not in OCS van der Walls complexes.\(^{15}\)

Using a relatively powerful color center laser in combination with a multïpass device, and bolometric detection, we have successfully used the upper state MW-IR-DR technique to determine the lifetime in the \(v_1\) fundamental of the HCN dimer. We report here on the experiments that have determined this lifetime to be \(-1.7(5)\) \(\mu\)s. This is the longest measured lifetime for a hydrogen bonded complex (not counting upper and lower limits that differ by orders of magnitude), and provides a unique datum to test calculations that apply to systems with very small couplings between the vibrationally excited mode and the dissociation coordinate.

We show in this paper that a simple rate equation model predicts that our experiment should have had negligible signal-to-noise ratio (S/N) given the excited state lifetime and the length of time that molecules are pumped. In order to provide an explanation for our observation of a double resonance signal, we propose a model based upon coherent interaction of both radiation fields with the molecular beam.

II. EXPERIMENT

A. Hardware

The experimental method adopted here is an extension of the well established technique of molecular beam, optothermal detection, infrared spectroscopy. For a general description of the detection technique, the reader is referred to Ref. 17, whereas in Ref. 18 our implementation is described in detail. Here we will present a brief description of our setup, and highlight the modifications made in order to carry out the microwave-infrared double-resonance experiment.

The HCN dimers are produced by expanding a mixture of 2% HCN in helium (Matheson) through a room temperature, 50 \(\mu\)m diameter nozzle at a stagnation pressure of 4 bar. A molecular beam is extracted from the expansion by a 0.5 mm conical skimmer, placed 10 mm downstream of the nozzle. The beam is detected \(-44\) cm further downstream by a liquid helium cooled (1.5 K) bolometer (Infrared Laboratories). Between skimmer and detector the molecular beam is crossed with the horizontally polarized infrared laser beam in a plano-parallel mirror multipass.

The microwave radiation is launched from a \(P\)-band (12–18 GHz) waveguide to counter propagate the molecular beam, as illustrated in Fig. 1. The molecular beam passes through a \(2 \times 3\) mm (horizontal \(\times\) vertical) aperture machined into a waveguide \(E\)-bend. The microwave radiation entering the space between the multipass mirrors is polarized perpendicular to the IR, although reflections will tend to scramble the microwave polarization. A rotary-vane attenuator provides for adjustment of relative microwave power. Microwave radiation is produced by a sweep oscillator (Hewlett Packard HP 8350B) with a 0.01–26.5 GHz plug-in (HP 8359A). The fundamental frequency of the oscillator's internal YIG oscillator is measured by a
frequency counter (HP 5245L) equipped with a 3–12.4 GHz frequency converter (HP 5255A). The intermediate frequency (IF) output of the counter (0–0.2 GHz) is phase-locked to the output of a highly stable (1 in $10^8$) frequency synthesizer (PTS 300). Both the short- and the long-term frequency stability thus attained are on the order of several Hz, much better than the experimental resolution, which is typically on the order of 50 kHz, thus the broadening in the double resonance spectra.

The absolute microwave field strength inside the machine depends on the effectiveness of the transmission line which couples the microwave power into the space between the multipass mirrors, and this could be strongly frequency dependent, especially outside the nominal (12–18 GHz) fundamental band of the waveguide. Moreover, the intensity in the microwave reflections present in the interaction region is also frequency dependent. Consequently, our measurements at different frequencies cannot be compared with each other in terms of signal level and saturation effects. Moreover, even at the same frequency, it is conceivable that the amount of microwave power coupled into the machine changes over longer time spans.

For most of the measurements, the IR was locked on a molecular transition in the molecular beam by FM modulation of the laser and demodulation of the bolometer signal. This removes the long term drift in the laser, but not the free running linewidth of the laser which is on the order of several MHz. The dominant feature(s) in the laser frequency noise spectrum are believed to be caused by mechanical resonances in the color center laser around 440 Hz. We have also run MW-IR-DR measurements with the frequency jitter of the laser reduced by locking it to the side of a confocal etalon, and then locked the etalon to the molecular transition. This gave negligible improvement in S/N in the present experiment, but has proven important in double resonance work on molecules with much larger single resonance signal levels.

The microwave radiation is amplitude modulated at 280 Hz and the double-resonance signal is observed at this frequency with a phase-sensitive detector, while the microwave frequency is scanned repeatedly over the rotational transition. These scans are performed with a personal computer which controls both the frequency of the RF synthesizer and the data acquisition.

B. Double-resonance signal: The excitation mechanism

In this section we will discuss the different factors that determine our experimentally observed linewidth and the intensity of the double-resonance signal, relative to that of the infrared transition alone. We are interested in the situation as depicted in Fig. 2 where the microwave radiation induces a rotational transition in the vibrationally excited state of the van der Waals molecule.

Our first observation is that, since both the lower and the upper level of the microwave transition are dissociative, the lifetime broadening for this transition obeys the relation $\Gamma_{DR}=1/\tau$, where $\Gamma_{DR}$ is the full-width at half-maximum (FWHM) of the Lorentzian linewidth component and $\tau$ is the predissociation lifetime of the van der Waals molecule (which is assumed to not depend on the rotational quantum number). This compares to $\Gamma_{IR}=1/2\pi\tau$ for the infrared excitation alone and thus the double-resonance experiment is twice as sensitive to the vibrational predissociation as the pure infrared experiment.

The second observation is that the optothermal detector senses the total energy content of the molecular beam and that therefore, in the case of a dissociating molecule, it is more sensitive to the absorption of an infrared photon (which causes dissociation) than to that of a microwave photon (which does not) by the ratio of the kinetic energy/molecule to the energy of a microwave photon, by a factor $\sim 10^4$ in the present case. Given our S/N, it is clear we only detect microwave transitions to the extent that they change the number of infrared photons absorbed or, in the case of van der Waals molecules, the number of molecules dissociating before reaching the detector. We can also see that the spectral resolution of the double-resonance experiment is not limited by the infrared Doppler width. As will be discussed below, we have achieved linewidths in MW-IR-DR of $\sim 50$ kHz, over 100 times smaller than our IR linewidth. With improved collimation of the microwave field, we expect the instrumental linewidth, limited by time-of-flight broadening, to be on the order of 10 kHz.

The most simple view we could take of the MW-IR-DR pumping is the traditional rate equation approach. We then expect, in the case of strong saturation of a bound–bound infrared transition, that approximately one-half of the molecules in the lower level are transferred to the excited ($v_0$) vibrational level. If now we simulta-
neously saturate a rotational transition from the upper infrared level to a lower or higher rotational level, we expect to equilibrate the initial ground state population over three states, two of which belong to the vibrationally excited state. It therefore follows that in the limit of strongly saturating infrared and microwave fields the double-resonance signal observed by modulating the microwave radiation is $\langle -\rangle / \langle \rangle$ of the signal observed by modulating the infrared radiation (for a nondissociating upper vibrational level). In experiments on propyne [pumping the $P(1)$ infrared transition, and making the $J'=1-0$ rotational transition in the $v_1$ vibrationally excited state] we have observed double-resonance signals larger than this (up to $\sim 40\%$ of the corresponding infrared signal).

When we consider the case when the upper state dissociates while the molecules are being pumped, the expectation is that the lower level of the infrared transition should be nearly completely depopulated. More precisely, the signals expected in the limit of strong IR and microwave pumping are proportional to $1 - (1/2)e^{-t/2\tau}$ for modulation of the IR laser (without microwave radiation) and $(1/2)e^{-t/2\tau} - (1/3)e^{-t/3\tau}$ for modulation of the microwave radiation with c.w. IR pumping of the molecules. In these formulas, $t_p$ represents the total time the molecules interact with the infrared radiation ($\sim 30\,\mu s$ in our experiment) and $\tau$ is the excited state lifetime. In the limit that $t_p \gg t$, the expected double resonance signal is only $(1/2)e^{-t/2\tau}$ of the IR signal. Driving a microwave transition in the upper state reached by the infrared transition is expected to change out of which level the dissociation occurs, but not the fact that practically all molecules dissociate and thus do not reach the detector. Consider for example the case of a molecule with a predissociation lifetime of $1.7\,\mu s$ (as found for the $v_1$ excited state of the HCN dimer) pumped for $30\,\mu s$, then the double-resonance signal would be expected to be attenuated by a factor of $\sim 10^3$, which would bring it well below our detection threshold. Yet, we have observed such a double-resonance signal in the HCN dimer! In order to explain this observation, we believe we must invoke a novel mechanism for production of the double resonance signal.

This proposed mechanism is based upon a coherent interaction picture (after all, in absence of collisions in the molecular beam environment, the only “relaxation” process to be considered is dissociation itself). We would have liked to perform detailed calculations to confirm our model, but given the poorly characterized molecular beam–microwave interactions (as reflected in the poorly understood observed microwave line shapes, see below) this does not appear practical at present. Below we will provide an explanation based upon a model with fully coherent sources. While reality is likely not so simple, loss of coherence should make the results more like that predicted by the rate equation model, and thus would be expected to reduce the size of the signal predicted neglecting such processes. We must begin our explanation by first carefully distinguishing between homogeneous and inhomogeneous broadening mechanisms.

There are two sources of inhomogeneous Doppler broadening. The finite collimation of the molecular beam ($3.5\,\text{mrad}$) combined with the molecular beam velocity of $1.6 \times 10^3\,\text{m/s}$ gives a $2\,\text{MHz}$ wide transition width at $3300\,\text{cm}^{-1}$, even with orthogonal laser crossings. However, in order to have the laser beam enter the plano-parallel mirror multipass it crosses the molecular beam at a small angle away from normal, typically $\sim 2^\circ$. This results in a Doppler shift of the absorption frequencies of $\sim 20\,\text{MHz}$ and an additional broadening of $\sim 2\,\text{MHz}$, assuming a (parallel) velocity spread in the molecular beam of $\sim 10\%$. The convolution of these inhomogeneous effects with an estimated $3\,\text{MHz}$ frequency jitter of the infrared laser predicts an inhomogeneous linewidth of $\sim 4\,\text{MHz}$.

When the molecular beam crosses a monochromatic, Gaussian laser beam the molecules experience the same Gaussian frequency spectrum, anywhere in the diffraction Gaussian laser beam. This Gaussian has a spectral intensity profile with a FWHM equal to $\delta v_G = (2 \ln 2)^{1/2} \nu_0 \sigma_0$, where $\nu$ is the molecular beam velocity, and $\sigma_0$ is the beam radius at the waist. In our experiments a $500\,\text{mm}$ focal length lens focuses the infrared laser into the multipass cell. Given a $3\,\text{mm}$ spot size on the lens, the diffraction limited spot size at the focus is $0.15\,\text{mm}$. This translates into a homogeneous Gaussian broadening of $4\,\text{MHz}$, and combined with the inhomogeneous linewidth yields a total linewidth $\sim 6\,\text{MHz}$, only slightly less than the $7-8\,\text{MHz}$ linewidth we observe experimentally.

However, the molecules are not subjected to a single laser crossing, but to a large number of them ($\sim 50$). For perfect parallelism of the multipass mirrors, each crossing presents the molecules with the same electric field distribution (for the reasons outlined above), but each delayed by a time $t_m \approx 1\,\mu s$. Because of this periodic modulation of the interaction with the infrared radiation, a spectral line profile is produced that consists of a series of peaks (Ramsey fringes) separated by $f_m = 1/t_m \approx 1\,\text{MHz}$ and extending over the $4\,\text{MHz}$ homogeneous width we calculated for a single crossing. The width of each individual peak will be the inverse of the total interaction time with the infrared radiation field, i.e., $\sim 30\,\text{kHz}$. Notice that if the lifetime broadening of the infrared transition $\Gamma_{IR} = 1/2\tau$ is less than $f_m$ the radiation will tend to burn “holes” in the inhomogeneous distribution of molecules, but that if it is greater than $f_m$ the entire inhomogeneous width will be pumped. Physically, this is just the requirement that in order for the multipass to have an effect on the excitation spectrum, the molecules must survive from one crossing to the next. The inhomogeneous Doppler broadening causes the Ramsey fringe pattern to be displaced in frequency for each selected velocity group. The combined effects of the inhomogeneous broadening mechanisms (Doppler and laser jitter) will be that the Ramsey fringes become undetectable in the current experiment, as they are washed out by the inhomogeneous distribution of molecules. Of course, the same is true for other coherence effects, such as Rabi oscillations, that otherwise might be observable.

Let us now consider the effect of driving a microwave transition in the vibrational upper state. This can be viewed as an A. C. Stark splitting of the infrared transition into
two peaks separated by the microwave Rabi frequency $\Omega_{\text{MW}}$. Each component of the infrared transition will have a transition dipole moment, and thus an IR Rabi frequency $\Omega_{\text{IR}}$, reduced by $\sqrt{2}$ compared to the single transition without the microwave field. For weak pumping of the infrared transition (in which case the excitation is proportional to $\Omega_{\text{IR}}^2$) the total absorption probability averaged over the inhomogeneous profile is independent of the microwave radiation field. But as the infrared laser saturates and burns a hole in the inhomogeneous profile, the presence of the microwave field will allow twice as many holes to be burned. For a stable upper state (no lifetime broadening), the width of each hole is proportional to $\Omega_{\text{IR}}$, and thus in the limit of a strong microwave field we expect a double-resonance modulation of $(2J/2J-1) = 41\%$ of the infrared signal. When the upper state dissociates, the width of the holes will be proportional to the convolution of $\Omega_{\text{IR}}$ and $\Gamma_{\text{IR}}$. Both the signal in the case of IR pumping alone, and the signal with the microwave radiation present will be larger when the upper state dissociates. But if the infrared transition is pumped too strongly, the width of the holes will grow to fill the $f_m$ gaps between the fringes in the excitation spectrum and vibrational predissociation will lead to a complete depopulation of the lower level of the infrared transition, regardless of whether or not the microwave radiation is present.

Lastly, we will consider the effect of power broadening. When the microwave power is reduced such that $\Omega_{\text{MW}}$ becomes smaller than the homogeneous width associated with the “holes” burned by the IR laser, the intensity of the double-resonance signal decreases rapidly, yet it is only in this limit that the linewidth observed in MW-IR-DR will accurately reflect the dissociation rate. One may also expect that $\Omega_{\text{IR}}$ would contribute to an infrared power broadening of the microwave transition, yet this is not observed; the minimum microwave resonance width, observed by scanning the microwave frequency around the rotational transition in the (vibrationally excited) upper state, does not decrease when the intensity of the infrared radiation is reduced. Just as for the case above, the microwave transition should not be broadened by the infrared power, but instead suffer an A. C. Stark splitting of the transition frequency proportional to $\Omega_{\text{IR}}$. This splitting is modulated periodically in time as the molecules fly through the multipass cell, resulting in a frequency modulation at $f_m$ of the microwave transition frequency. One would therefore expect microwave absorption at detunings equal to multiples of $f_m$. However, due to partial overlapping of the laser beam inside the multipass cell, the modulation index must be rather low. These sidebands appear to be too weak to be detected with the current experimental configuration.

### III. RESULTS

#### A. Ground state spectra simulation

In order to understand the microwave line shapes observed in our experiments it is useful to compare the experimentally observed transitions between two rotational levels of the ground state of (HCN)$_2$ (when one of these is coupled to an upper, rovibrational state) to a simulated spectrum.

Table I lists the calculated transition frequencies and the corresponding relative absorption intensities calculated for the $J = 3 \rightarrow 2$ and $J = 4 \rightarrow 3$ transitions. The coupling scheme used in the calculation of the quadrupolar hyperfine structure first adds the electric quadrupole moment $I_1$ on molecule “1” to the rotational angular momentum $J$ of the dimer, and subsequently couples the resulting vector $F_1$ to the quadrupole moment $I_2$ on the other HCN molecule to yield the total angular momentum $F$. Since there will be several (nondegenerate) states for each combination of $J$ and $F$, we report in Table I also the expectation value of $F_1$ (which is generally not a good quantum number). Our calculation does not take into account second-order quadrupole effects, in effect assuming that $J$ is a good quantum number. This is expected to be a very good approximation, as the magnitude of the $^{14}$N quadrupole coupling constant ($\sim 4$ MHz) is much smaller than the rotational constant $B$ (1746 MHz).

In order to construct the simulated spectrum we will need to convolute the stick spectrum based on Table I with the instrumental line shape. In principle, this function can be directly obtained by recording a single transition that does not show any fine structure or other machine-independent broadening, such as the $J = 1 \rightarrow 0$ transition in propyne at 17 GHz. This transition, shown in Fig. 3, appears to be dominated by two features.

Of these we attribute the one at low frequencies to absorption arising from the microwaves launched directly from the waveguide and counterpropagating the molecular beam. This feature is observed at 17 091.685 MHz, or 60 kHz lower than the calculated transition frequency based on the rotational constants of Wlodarczak et al.

The Doppler shift that results from the counterpropagation, assuming a mean molecular beam velocity of 1600 m/s, is calculated to amount to 90 kHz, 30 kHz more than the observed shift. This may in part reflect both velocity slippage in the molecular beam and some calibration error of our microwave frequencies, but another likely contribution is that the wave front of the microwave radiation is not normal to the molecular beam.

The feature to the high frequency side is thought to be caused by reflected microwave radiation, coming from either the multipass cell, or perhaps the back wall of the vacuum chamber. This is supported by the frequency separation between the two features (124 kHz) which is in fair agreement with the estimated Doppler shift of $\pm 90$ kHz for co- and counterpropagation of the microwaves relative to the molecular beam. This splitting certainly does not arise from A. C. Stark splitting associated with either the microwave or IR radiation field, since the size of the observed splitting is independent of both IR and microwave power. The intensity in the highest frequency feature is around 75% of that in the main feature, while both have approximately the same FWHM of $\sim 75$ kHz. We have observed about the same fractional linewidth ($\sim 4$ ppm) on MW-IR-DR transitions for a number of molecules, as

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TABLE I. Calculated transition frequencies and intensities for the $J=3\cdot2$ and $J=4\cdot3$ rotational transitions in (HCN)2. The molecular constants used in the calculation, and reproduced here, are from Buxton et al. (Ref. 23). The transitions reported here have an intensity $>0.01$.

\[
e_{\text{Q}^a} = -4.0973(200) \text{ MHz}
\]
\[
e_{\text{Q}^b} = -4.4400(190) \text{ MHz}
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B=1745.80973(50) \text{ MHz}
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*aRefers to the N nucleus participating in the hydrogen bond.

*bRefers to the nonbonded N nucleus.

expected if the width of each feature is due to Doppler broadening.

These observations have led us to convolute the calculated transition frequencies and intensities of Table I (the stick spectrum shown in Fig. 4) with an "apparatus function" composed of the sum of two Gaussians of equal width but variable height, and a variable spacing reflecting the Doppler shift between the two microwave components described above. The simulated spectrum obtained in this way was fitted to the experimental ground state $J=3\cdot2$ transition in the HCN dimer, which shows the best S/N and resolved hyperfine structure at a very low microwave power level. The result is presented in Fig. 4(a). The significant parameters obtained from the fit are the Gaussian
width of 48.4(4) kHz (FWHM), the separation of the two Doppler components of 55.7(6) kHz, and the intensity in the absorption(s) associated with the reflected microwaves relative to that associated with the main counterpropagating component, 58(2).% The uncertainties given in parentheses represent twice the standard deviation obtained from the least squares fit. The fitted separation of the two Gaussian components is in excellent agreement with a Doppler shift of 56 kHz for a molecular beam velocity of 1600 ms⁻¹. A linewidth of 46 kHz is predicted based upon scaling of the observed propyne linewidth. The separation of the two components is likewise predicted to be 76 kHz, somewhat larger than observed. The difference between the measured and calculated (based on the microwave data of Buxton et al.) transition frequencies equals 25 kHz, about half the expected Doppler shift, just as was observed for the propyne measurement. The fit is surprisingly good in view of the fact that at first sight the simulated stick spectrum shows a poor resemblance to the experimental spectrum. In particular, the intensity alternation observed for the (six) strongest transitions in the stick spectrum appears to be exactly the opposite of what must be observed in our experiment.

Figure 4(b) shows the result of a similar fit to the J=4 ground state transition. The result is less satisfactory, in that the fit requires a rather large Gaussian width of 110 kHz (FWHM) to fill the gaps between the narrow features present in the spectrum (a width of 61 kHz is expected based upon the propyne measurement). Also, the intensity in the absorption associated with the microwave reflections appears to be much lower (22%) than for the propyne measurement. The fit is surprisingly good in view of the fact that at first sight the simulated stick spectrum shows a poor resemblance to the experimental spectrum. In particular, the intensity alternation observed for the (six) strongest transitions in the stick spectrum appears to be exactly the opposite of what must be observed in our experiment.

B. Upper state rotational constants

The observation of rotational transitions in the vibrationally excited state presents the possibility to obtain more accurate rotational constants for the v₁ bands of the (HC₁⁴N)₂ and (HC₁⁵N)₂ dimers. The difference in the frequencies at which we observe the ground state and the upper state MW-IR-DR transitions is a direct measure for the value of AB.

For the ¹⁴N isotopic species we have data on both the J=3 and the J=4 upper state rotational transitions. The experimental J=3 and upper state microwave frequencies yield a ΔB = -1.395(6) MHz, while the J=4 frequencies give ΔB = -1.157(5) MHz. The estimated uncertainties mostly reflect the uncertainty in the frequency measurements.
exact center of the (power broadened) upper state transitions, averaged over several measurements. This transition frequency was determined by fitting the upper state spectra to a (very low power) ground state spectrum (which includes the hyperfine structure in the case of the HC\textsuperscript{14}N dimer), convoluted with a Lorentzian that reflects the power broadening present in the upper state, as will be described in more detail when we discuss the determination of upper state lifetimes in the next section. The difference in these two values for $\Delta B$ is clearly much larger than the experimental uncertainty. This is most likely a sign of a local perturbation in the spectrum. In the absence of more data, it is difficult to say with certainty which of the three levels involved in the transitions measured here is most affected by the perturbation. However, the $\Delta B$ value determined from the $J=4 \rightarrow 3$ transition, $-1.157(5)$ MHz, turns out to be in fairly good agreement with $\Delta B = -1.178(18)$ MHz were obtained from a fit to 55 transitions observed in the IR spectrum of the dimer by Jucks and Miller.\textsuperscript{12} In this fit, $B''$ was constrained to the microwave value of Buxton et al.\textsuperscript{23} The perturbation in question therefore seems to shift the $J''=2$ level more than either the $J''=3$ or the $J''=4$ level. Although it is certainly not exactly true, we will assume the $J''=2$ level to be the only perturbed level of the three. In this case the perturber appears to have pushed this level up in frequency by an amount of $6 \cdot (-1.157+1.395) = 1.43$ MHz, well within the accuracy with which the IR line positions were determined. As we will see below, the conclusion of a localized perturbation being present is supported by the observation of slightly different lifetimes as obtained from the $J=3 \rightarrow 2$ and the $J=4 \rightarrow 3$ transitions in (HC\textsuperscript{14}N)\textsubscript{2}.

For the HC\textsuperscript{15}N dimer we have observed an upper state rotational transition for $J=4 \rightarrow 3$ only. The value for $\Delta B$ determined from this datum is $-1.023(3)$ MHz. This compares to $-1.076$ MHz obtained from the scaling relation, $\Delta B'_2 = \text{constant}$.

C. Upper state lifetime measurement

The presence of hyperfine structure in the microwave (infrared double-resonance) spectra of the dimer and of power broadening induced by the microwave field complicates the determination of the contribution of lifetime broadening to the linewidth of the vibrationally excited state. Both microwave power and lifetime broadening result in a Lorentzian component to the measured line profile for an upper state rotational transition. We can approach the problem of separating these two contributions in two ways.

First we can attempt to extrapolate the higher power measurements down to zero microwave field strength. In this scheme we determine the total Lorentzian component to the upper state spectrum by deconvolution of this measurement with a low power ground state measurement. The latter should account for both the hyperfine structure and the instrumental line shape, i.e., the Gaussian broadening (dominated by interaction time broadening) and the effect(s) of microwave reflections. Note that this implicitly assumes that the quadrupole hyperfine constants do not noticeably change upon vibrational excitation of the $v_1$ mode. The total Lorentzian component is then the convolution of just the power and lifetime broadening effects.

Figure 5 compares the $J=3 \rightarrow 4$ upper state spectrum recorded at a (relative) microwave power level of $-10$ dB, with the observed $-21$ dB, $J=4 \rightarrow 3$ ground state double-resonance spectrum convoluted with a 325 kHz Lorentzian. Since the Lorentzian width resulting from power broadening depends linearly on the electric field strength, we have chosen to plot in Fig. 6(a) the total Lorentzian component as a function of the relative electric field strength for three such measurements carried out on the $J=4 \rightarrow 3$ transition in the dimer, and one set of data for the $J=3 \rightarrow 2$ transition [Fig. 6(b)]. The data were obtained in different runs, but if the absolute microwave power levels are the same (i.e., $E_0$ is constant) we can combine the $J=4 \rightarrow 3$ measurements to yield a zero-power Lorentzian component of 159(50) kHz (FWHM), corresponding to an upper state lifetime of 2.0(6) $\mu$s. The differences between the data recorded in different runs most likely reflect systematic errors in the experiment and its analysis. For example, it is observed that the lowest S/N measurements consistently tend to overestimate the linewidth. In the case of the $J=3 \rightarrow 2$ transition the zero field intercept yields a lifetime broadening component of 192(74) kHz (FWHM), indicating a lifetime of 1.7(6) $\mu$s. Once more the quoted uncertainties represent $2\sigma$, as obtained from the least squares fit to the data.

A second approach determines the Lorentzian lifetime component of the upper state double resonance spectrum by fitting to a line shape consisting of a convolution of a Lorentzian of adjustable width with the observed ground state double resonance signal obtained at the same microwave power. The power broadening contribution to the width should be the same in both spectra assuming we can neglect the change in dipole moment with the vibrational

\begin{figure}[h]
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\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{Example of an upper state MW-IR-DR signal for the HC\textsuperscript{14}N dimer $J=4 \rightarrow 3$ transition at a relative power level of $-10$ dBm ($E/E_0 = 0.32$). The fitted curve is a convolution of the $-21$ dBm ground state spectrum with a 325(10) kHz Lorentzian. The ground state spectrum was observed over a 1500 kHz interval only. The fit was therefore restricted to the range from 900 to 2400 kHz in the figure.}
\end{figure}
quantum number (and the change in microwave frequency is sufficiently small that significant changes in the effectiveness of the coupling into the apparatus are not expected). Results of this type are presented in Fig. 7 for the $J=4\rightarrow3$ and $J=3\rightarrow2$ transitions. The average Lorentzian component is 208(42) kHz for the $J=4\rightarrow3$ measurements. This value corresponds to a 1.5(3) μs lifetime, in agreement with the lifetime of 2.0(6) μs obtained by the first method. Here it should be noted that again the low-power measurements are afflicted with a low S/N, while the higher power measurements could become less and less sensitive to the lifetime broadening as the power broadening starts dominating the spectra. Despite this, the results for the $J=3\rightarrow2$ transition show an unexpectedly large residual power dependence, that in principle should have been eliminated by the method used here to analyze the data. Clearly, at the highest microwave power levels in our experiment the upper state spectrum broadens much faster than expected from (ground state) power broadening alone. We therefore have elected to ignore the higher power measurements and find for the remaining data an average Lorentzian component of 387(28) kHz. In this case the uncertainty corresponds to 2σ, and does not reflect the uncertainty in the linewidth determination resulting from a poor S/N. Considering the experimental S/N of these measurements we will take as a more realistic estimate of the Lorentzian component a value of 390(60) kHz which would correspond to a lifetime of 0.82(12) μs, somewhat shorter than the result obtained with the first method of analysis, 1.7(6) μs.

We have also been able to obtain several spectra on the $J=4\rightarrow3$ transition in $(\text{HC}^{15}\text{N})_2$, which shows no quadrupole hyperfine structure ($I=0.5$ for $^{15}\text{N}$). Unfortunately, after several quick ground state MW-IR-DR scans at different power levels with the IR laser tuned to the $R(3)$ transition in the dimer, we experienced serious difficulties in finding DR signals on the accompanying upper state microwave transition. Only after tuning the IR laser to the $P(4)$ transition, we were able to observe the upper state $J=4\rightarrow3$ spectrum. At that time our gas sample was nearly depleted and the spectrum was obtained at only one microwave power level. Still, it is possible to estimate the amount of power broadening present in this upper state
FIG. 8. The widths of the Lorentzian components of the ground and upper state MW-IR-DR spectra for the \( J'=4-3 \) transition in \((\text{HC}^{'\text{15}}\text{N})_2\) as a function of the MW electric field strength.

spectrum, if we can assume that the power broadening coefficients and the absolute power levels before the attenuator are the same for both the ground state and the upper state measurements. For the reasons given in the discussion of the \((\text{HC}^{'\text{14}}\text{N})_2\), \( J=4-3 \) data, we believe that this is a reasonable thing to do. The Lorentzian power broadening component for each measurements was obtained assuming that the double-Gaussian, experimental line profile resembled that obtained for the \((\text{HC}^{'\text{14}}\text{N})_2\), \( J=4-3 \) (ground state) measurement of Fig. 4(b). Figure 8 shows the Lorentzian linewidths as a function of the electric field strength and the extrapolation of the upper state measurement to zero-power based on the power dependence of the ground state Lorentzian components. This procedure results in an estimate of the lifetime broadening for the DR signal of \( \sim 280(100) \) kHz and a \( 1.1(4) \) \( \mu \)s lifetime. Here the estimate for the error bar is based on the scatter observed in the data of Figs. 6(a) and 7(a).

IV. DISCUSSION

Here we will take a closer look at the \( J=3-2 \) measurements. By measuring both the \( J'=3-2 \) and the \( J'=4-3 \) upper state transition frequencies with microwave accuracy we have established a perturbation that is predominantly shifting the \( J'=2(v=1) \) level. The presence of this perturbation raises the possibility that the vibrational predissociation lifetimes of the levels probed by our experiment are not all the same. Both our methods of analysis indicate that the \( J'=3-2 \) transition is broader than that for \( J'=4-3 \), though only for the second method is the difference predicted to be statistically significant. Unfortunately, the 2\( \sigma \) error bars of the two methods of analysis do not overlap, so the differences in linewidth of the two microwave transitions must be viewed as likely but not certain. One possible cause of difficulty in our analysis is the assumption that the quadrupole splitting is the same in the ground and upper state. We believe that this should be a good approximation for the pure \( \nu_1 \) fundamental, but if this state is mixed with another which has quanta in the intermolecular bending modes, then the effective eqQ's should be significantly reduced.

At this point we can only speculate about the cause of the unexpected broadening observed at the highest power levels in the \( J=3-2 \) spectra. So far we have assumed that the interaction responsible for the perturbation is long range and presumably anharmonic in nature. But the perturbed level \( (J'=2) \) is (slightly) displaced and requires a relatively small amount of the “dark” state character. Only if this latter state is intrinsically much broader would we expect to see an appreciable lifetime broadening of the “bright” state. Also, the “dark” state requires little transition strength and, if at all, appears in the spectrum far from the zeroth-order state. This scheme appears to be the most reasonable considering the very low density of vibrational states of the dimer. It is at least in theory conceivable that the perturbation is of a much more resonant nature. In that case the expected zeroth-order state will appear split into two components in the spectrum. If this splitting were small, say \( \sim 2 \) MHz, this would go undetected in the pure IR spectrum. But at the same time it becomes possible that we start seeing the “dark” state in the double-resonance spectrum when the power broadening approaches the size of the splitting. Obviously, this could result in an apparent increase in the Lorentzian broadening of the spectrum. Since the \( J'=2 \) level appears to have been pushed up in frequency by the perturbation, the “dark” state would have to be lower in frequency than the \( J'=2 \) level. It would therefore appear at the high-frequency side in the \( J'=3-2 \) spectrum. Unfortunately, the high-power \( J=3-2 \) spectra extend over 6 MHz, while the low-power spectra extend over only 2 MHz, where they show no sign of a possible perturbing state. Another, and perhaps more likely, possibility is that the wings of the (microwave power broadened) ground state spectrum become visible at the highest power levels (the separation between upper and ground state spectra equals 8.4 MHz).

The above also forces us to take another look at the analysis of the \( J=3-2 \) data as presented in Fig. 6(b). There we obtained a 197(74) kHz Lorentzian component by extrapolating the measurements at different power levels down to zero microwave field. Besides the problems with the higher power measurements identified above (that will also influence the result of this analysis), there is another possible problem with analyzing the data in this way, which is that the upper state spectra could be severely affected by saturation effects at the higher microwave power levels. This is because at higher microwave power levels the hyperfine components with the largest dipole moment matrix elements will become saturated, therewith increasing the relative intensity of the weaker components in the spectrum. As a result, the overall intensity distribution of the upper state spectrum could become very different (most notably wider) from that observed for the much lower power ground state measurement. Deconvolution of such an upper state measurement would yield a Lorentzian width that at the very least overestimates the lifetime broadening, if the least-squares approximation converges


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at all. Within the accuracy of our measurements, there appears to be no reason to assume this is actually the case for the $J=4 \to 3$ measurements. However, in the case of the $J=3 \to 2$ measurements it appears that perhaps indeed the linewidths increases faster than linear at the highest (relative) power levels.

It may therefore be clear that also in this case we should determine the zero-power Lorentzian component for only the lowest power measurements, which yields a value of 317(60) kHz.

In conclusion, we believe that despite the difficulties with the $J=3 \to 2$ measurements, the lifetime broadening for this upper state transition is likely significantly larger than for the $J'=4 \to 3$ transition. A reasonable estimate of the Lorentzian lifetime component appears to be 350(90) kHz (FWHM). Care must be taken in interpreting this linewidth in terms of a lifetime since it is associated with the decay of both the lower and the upper level of the microwave transition. However, the lifetime of the system can be estimated from the relation $\tau = 1/(2\pi r_2) + 1/(2\pi r_3)$, where in this case $r_2$ is the lifetime of the $J'=2$ level and $r_3$ the lifetime of the $J'=3$ level. If our hypothesis is correct and only the $J'=2$ rotational level is significantly perturbed then $r_2$ equals $\sim 2$ µs, and therewith $r_3=0.6 \mu$s for the $J'=2$ level. This shorter lifetime must result from coupling to an even shorter lived perturbing state.

On the basis of the $(\text{HC}^{14}\text{N})_2$ data we conclude that the unperturbed lifetime for the $v_1$ excited HCN dimer is best represented by

$$\tau = 1.7(5) \mu s. \quad (1)$$

We arrived at this value by taking the average of the results for the $J=4 \to 3$ measurements of Figs. 6(a) and 7(a). We note that, although the measurement itself is outside the error bar given with expression (1), the linewidth for $(\text{HC}^{14}\text{N})_2$ is not in disagreement with this value considering the large uncertainty in the measurement.

It is interesting to compare this lifetime to those of other (hydrogen bonded) complexes. A convenient and instructive way to do this uses the empirical correlation law first proposed by Miller, based on observations for a range of related systems (all containing at least one HCN or HF monomer unit).

$$\tau^{-1} \propto (\Delta \nu)^2, \quad (2)$$

where $\Delta \nu$ represents the (complexation induced) red shift of the vibration excited in the complex, with respect to the corresponding vibration in the monomer. This relation has been rationalized by LeRoy et al. in a first-order perturbative treatment for the much simplified case of only one internal degree of freedom. It was shown that the origin of the correlation law can be found in the fact that both phenomena (red shift and vibrational predissociation rate) are driven by the same terms in the intermolecular potential. In Fig. 9 we have reproduced Miller's figure on a logarithmic scale [a natural choice not only given Eq. (2), but also because the predissociation rate spans at least 6 orders of magnitude for the systems that have been studied so far]. Our result, $\log_{10}(\tau^{-1}) = 5.77(13)$, and the red shift $\Delta \nu = 3.16 \text{ cm}^{-1}$ measured previously for the $v_1$ band in the dimer, place the $v_1$ excited dimer somewhat outside the band formed by the other systems (it being longer lived than "predicted"). In contrast, for the CH stretch of HCN-HF (Ref. 26) the lifetime is substantially shorter than would be predicted on the basis of the correlation law. Both these systems show red shifts that are very small compared with the other data, indicative of a very weak coupling between the excited vibration and the dissociation coordinate. One could take the position that such a weakly coupled system should lend itself well for a first-order perturbative treatment. This has been essentially the basis for the arguments presented in Ref. 11, where we extended the model of LeRoy and co-workers to include overtone excitation of the intramolecular, high-frequency vibration (the CH stretch in HCN-HCN and HCN-HF). We found that the experimentally observed ratio of the overtone to fundamental $v_1$ red shift of (HCN)$_2$ agrees very well with the ratio predicted by the model. The same is true for the ratio of the overtone to fundamental $v_2$ lifetime of HCN-HF. But the ratio of red shifts in this case does not agree so well, which was attributed to a long-range anharmonic vibrational interaction in the dimer. Such a perturbation of the vibrational levels would have no direct bearing on the vibrational predissociation lifetimes (unless of course, the perturber is intrinsically "much" broader). Of course, one could also take the view that such small effects are determined by a cancellation of larger terms and that consequently the excellent agreement between such a simple theory and some of the experimental results could be fortuitous. LeRoy and co-workers have shown that this is to be expected when their model is extended to allow for more than one internal degree of freedom.25 They have
postulated that the persistence of the correlation law for a range of related systems is therefore implicit evidence of a two-step impulsive predissociation mechanism in which the initial rate-determining step involves only one internal degree of freedom. The redistribution of the released energy over the internal degrees of freedom of the fragments is then decided during the process of fragment separation. This mechanism is fully supported by state-to-state vibrational predissociation measurements of the \(J-J\) correlations in the product distributions of the HF dimer.\(^{27}\) More recently it was shown that the same experimental technique could be applied to the HCN dimer, albeit with a loss of true final state resolution.\(^{28}\) It is evident that a quantitative understanding of the vibrational predissociation mechanisms will only be possible with the aid of accurate theoretical calculations performed on realistic multidimensional potential energy surfaces.

V. CONCLUSIONS

Vibrational interactions have been observed in the IR spectra of a fair number of small complexes studied to date. In all these cases, the perturbations are very localized in nature, and generally affect a few rotational levels at a time. Our results, indicating a small perturbation affecting primarily one rotational of the HCN dimer is entirely consistent with this previous body of data. The perturbation shifts the \(J' = 3 \rightarrow 2\) rotational spacing and likely leads to enhanced dissociation as well. The existence of hyperfine structure with splittings comparable to the homogeneous linewidth limits the precision of the lifetime determination. It would have been interesting to extend the measurements to transitions between higher rotational levels because of the rapid decrease in quadrupole splitting with \(J\). We have attempted to record the \(J = 5 \rightarrow 4\) transitions, but only succeeded in observing the ground state MW-IR-DR signal.

Some substantial improvements can be made to our experimental setup. These modifications will result in a better defined molecule–radiation interaction. This should allow us to make detailed comparisons of observed and calculated MW-IR-DR signals, which we expect will allow us to critically test the coherent double resonance mechanism proposed in this paper.

ACKNOWLEDGMENTS

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2. See, e.g., R. E. Miller, Acc. Chem. Res. 23, 10 (1990), and references therein.