Spectroscopy of Pendular States: The Use of Molecular Complexes in Achieving Orientation

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Infrared-laser–molecular-beam spectroscopy has been used to observe strongly bound pendular states of the linear hydrogen cyanide trimer. The spectrum undergoes a dramatic evolution from that of a free rotor at zero electric field, with its characteristic P and R branch structure, to that indicative of a pendulum bound by a large electric field (corresponding to $\omega = \mu E/B = 365$). The result is an unprecedented degree of orientation for a linear molecule. The generality of using weakly bound complexes to orient even nonpolar molecules is discussed.

Despite the fact that steric effects are of fundamental importance in essentially every branch of chemistry, experiments designed to measure them under single-collision conditions are still problematic. The difficulties arise from the fact that, to obtain information of this type, the reagents, which are spread over a distribution of rotational states, must be oriented in some way prior to the collision. To date, there are still no completely general methods available for achieving this goal. For the case of a polar symmetric top, some degree of orientation can be achieved using electric focusing fields, as first demonstrated by Bernstein and co-workers [1,2] and Brooks and Jones [3]. Indeed, a large number of studies on the steric effects associated with symmetric tops have been carried out in both crossed molecular-beam experiments [2–7] and gas-surface collisions [8–11]. As discussed by Estler and Zare [12], polarized laser excitation can be used to align molecules, owing to the fact that they are preferentially excited if the electric transition moment is aligned with the laser electric-field direction. This method has been applied in various forms by a number of groups for studying steric effects [13–18].

Very recently there has been considerable interest in using large, uniform electric fields to orient molecules by virtue of the fact that an electric dipole experiences a torque in the field. Normally this torque is considered small with respect to the molecular rotational energy [19], such that the corresponding effect on the rotational wave functions, and hence the molecule's average orientation, is negligible. However, as pointed out by Herschbach and co-workers [20–22] and Loesch and Remscheid [23], the effect can be greatly enhanced if the molecules are cooled to low rotational temperatures using a free jet expansion. For systems with large dipole moments and small rotational constants, experimentally realizable electric fields can give rise to significant orientation. These two groups have done extensive calculations that show the feasibility of this technique, and Loesch and Remscheid [23] have used this method for orienting CH_3I to examine steric effects in the reaction $K + CH_3I \rightarrow KI + CH_3$. Friedrich and Herschbach [22] have reported laser-induced fluorescence experiments on ICl at fields up to 20 kV/cm and an assignment of the resulting Stark spectrum confirms that, at these field strengths, the lowest rotation-

al states are beginning to become pendular. To date, however, there have been no spectroscopic measurements on systems in the limit where the interaction with the electric field completely dominates over the rotational energy, such that the molecules are strongly bound in these pendular states and highly oriented with the field.

We report here a high-resolution infrared study of the pendular states of the linear HCN trimer [24,25], which is ideally suited to this type of study owing to its large dipole moment (10.6 D [25]) and small rotational constant (0.0156 cm^{-1}). For this system we are able to make $\mu \cdot E$ large in comparison with $BJ(J+1)$ for all of the states populated in the molecular beam. As the electric field is increased the infrared spectrum evolves from the normal P and R branch structure of a linear molecule into a rather confused spectrum, due to the lifting of the m_J degeneracies. At even higher fields the spectrum simplifies again when all of the populated states become essentially harmonically bound by the field. In this high-field limit many of the states become degenerate again and the spectrum is easily assigned in terms of the selection rules associated with these harmonic-oscillator-like states.

The experimental apparatus used in the present study has been described in detail elsewhere [26–28]. It is based upon the use of the optothermal detection technique [29], which provides high-sensitivity infrared spectra of free-jet–cooled molecules. The gas of interest is expanded from a nozzle source, collimated by a skimmer to form a molecular beam, and detected by a liquid-helium–cooled bolometer detector. An F-center laser is used to vibrationally excite molecules in the beam while the bolometer monitors the resulting change in the molecular-beam energy. This change can result from either the vibrationally heating of the molecules in the beam or the depletion of the beam due to photodissociation of the excited species, which leads to recoil of the fragments out of the line of sight of the bolometer. In the present setup, the laser interacts with the molecular beam between two Stark electrodes, which act as both a parallel reflection cell for increasing the number of laser–molecular-beam crossings [30] and a means for applying a uniform electric field to the interaction volume. As shown in Fig. 1 the laser electric-field vector is approxi-
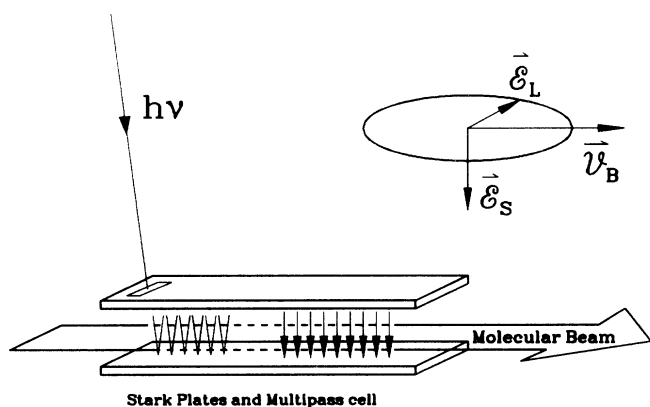
FIG. 1. A schematic diagram showing the geometry of the laser–molecular-beam crossings. The gold-coated glass plates provide multiple crossings as well as the uniform electric field. The laser enters the Stark cell through the slot in order to ensure that the field is uniform for all of the crossings.

FIG. 2. A series of optothermal spectra showing the transition from free-rotor behavior to that characteristic of pendular motion.

mately perpendicular to the static electric field, making the relevant selection rule $\Delta m = \pm 1$ [19]. The present design of the Stark cell can be used to provide electric fields up to approximately 30 kV/cm. For the hydrogen cyanide trimer this corresponds to $\omega = \mu E/B = 365$, which places the system well within the pendular regime for all of the populated rotational levels. As a point of comparison, the highest value of ω achieved previously (for ICl) was 4 [22]. It is also interesting to note that at this field strength the barrier to free rotation is 11.4 cm^{-1}, compared with $B = 0.015$ cm^{-1}. This is clearly sufficient to trap states up to quite large J.

Since the rovibrational spectrum of a molecule is directly sensitive to the spacing between rotational energy levels, it can be used to directly probe the influence of the electric field on these states. Figure 2 shows a series of such spectra as a function of the applied electric field. The molecular beam was formed by expanding a 1% mixture of HCN in helium through a room-temperature 50-μm-diam nozzle from a source pressure of 400 kPa. The vibrational band examined in this study corresponds to the asymmetric combination of hydrogen-bonded C-H stretches [24]. At zero field the spectrum shows the expected P and R branch structure of a linear molecule. The transitions are considerably broader than the instrumental resolution as a result of the rapid vibrational predissociation which occurs upon laser excitation [24]. Careful examination of the intensity distributions observed in this zero-field spectrum reveals that the rotational temperature of the trimer is approximately 2 K.

At moderate electric fields the central part of the spectrum becomes highly congested. This is a result of the fact that the applied field lifts the m_j degeneracies (note that the $\pm m_j$ degeneracy remains) so that the number of allowed transitions increases dramatically. At the same time, the higher J transitions are essentially unaffected by the field, since the associated rotational energy is large
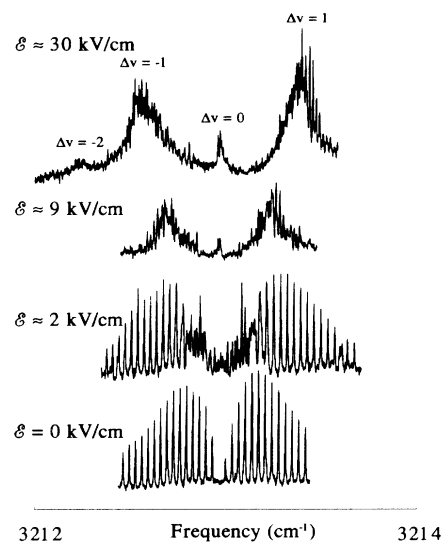
in comparison with μE. An interesting transformation occurs as the applied field is increased further. At 15 kV/cm all of the transitions are highly perturbed by the field and they begin to group together in clumps, which then move apart as the field is increased further. In addition, transitions appear at the vibrational origin, which obviously cannot be explained in terms of the selection rules for a freely rotating linear rigid rotor ($\Delta J \neq 0$). It is interesting to note that a regular progression of highly resolved transitions begins to appear in the spectrum at the highest fields. As we will now explain, this dramatic change in the appearance of the spectrum is directly related to the transition from free-rotor to pendular behavior.

The above spectra are best interpreted with the aid of a correlation diagram, shown schematically in Fig. 3, which is similar to those discussed earlier by Friedrich and Herschbach [20]. At the left of the correlation diagram are the free-rotor energy levels, designated by their rotational quantum numbers (J), while on the right are a set of equally spaced states representative of a harmonic oscillator. The harmonic description is clearly only valid at very high fields where the bottom of the $\mu E \cos \Theta$ potential is essentially harmonic. It is immediately obvious from this diagram why the spectrum becomes congested at moderate electric fields, corresponding to the system being near the center of the correlation diagram. Under these conditions the number of initial and final states is very large, giving rise to numerous transitions. It is interesting to note, however, that in the limit of very high fields, we begin to recover the degeneracies that were initially lifted by the electric field. This explains why the spectrum begins to simplify again at the highest fields, as indicated by the resolved structure which begins to reap-
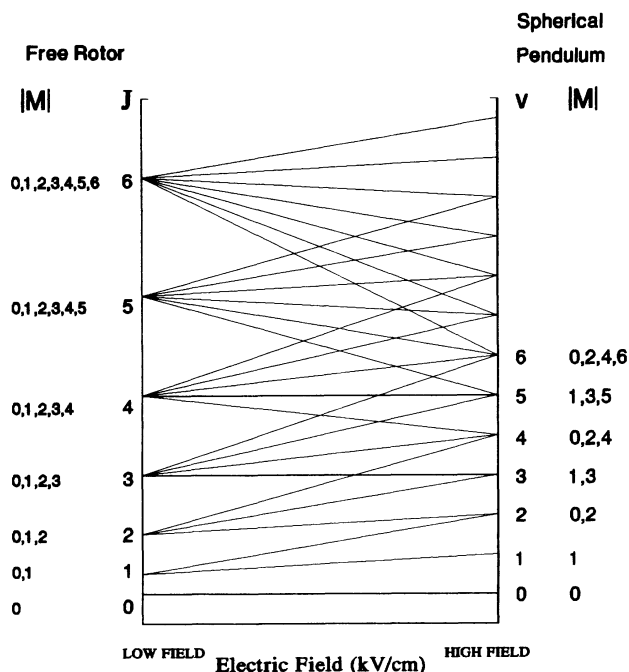
FIG. 3. A correlation diagram showing the connections between the low- and high-field limits. On the left of the diagram are the free-rotor states which evolve into the harmoniclike pendular states at high field.
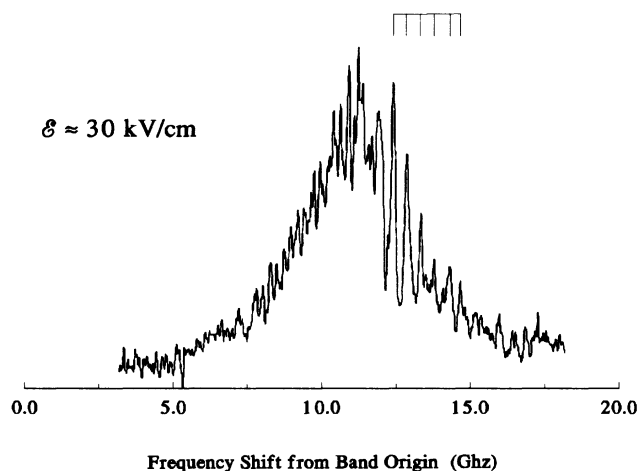

FIG. 4. An expanded view of the $\Delta v = +1$ band, showing the resolved progression at large frequency shifts, corresponding to the lowest-energy pendular states.

pear. In the harmonic limit, all of the pendular states will become equally spaced and transitions between the ground and excited vibrational states with the same Δv (v being the harmonic quantum number describing the pendular states) will have the same frequency. With this in mind, it is straightforward to make the Δv assignments given in Fig. 2, which shows four bands corresponding to $\Delta v = 0$, ± 1, and -2. It is clear from the fact that these bands are not delta functions in frequency that we have not yet reached the harmonic regime. Indeed, the $\Delta v = \pm 1$ bands have tails extending toward the band origin, indicative of the fact that the states higher up in the potential are more closely spaced, owing to the anharmonicity associated with the $\mu E \cos\Theta$ potential.

It is evident from the correlation diagram that the $\Delta v = 0$ transitions correlate with $\Delta m = 0, \pm 2, \pm 4, \ldots$, which are not allowed when the electric vector of the laser is precisely aligned perpendicular to that of the static field. As noted above, however, the laser–molecular-beam crossing must be aligned slightly nonorthogonally in order to get the laser to multipass between the Stark electrodes. In the spectra reported in Fig. 2 the laser polarization was at an angle of approximately 45° to the molecular beam so that this nonorthogonality gave rise to a small component of parallel polarization. Spectra have also been recorded with the laser polarization adjusted to be perpendicular to the molecular beam, thus ensuring that it is also perpendicular to the static field. Under these conditions the $\Delta v = 0$ band is no longer present, as

expected.

Figure 4 shows an expanded view of the $\Delta v = +1$ band at the highest electric-field strength of approximately 30 kV/cm. The well-resolved progression is to the high-frequency side of the band. Since this region of the spectrum corresponds to the largest frequency shift from the band origin, the associated states must be those which are deep in the potential, such that their harmonic frequencies are the highest. It is therefore clear why these states emerge from the congested band first, since they are the most harmonic states and are therefore the first to arrive at the right-hand side of the correlation diagram shown in Fig. 3. Once again, the splitting between the transitions is a result of the anharmonicity associated with the $\mu E \cos\Theta$ potential. This interpretation is confirmed by the fact that the frequency shift from the band origin is approximately 11 GHz for these transitions, which is in good agreement with the calculated value for the $v = 1 \leftarrow 0$ transition (11.8 GHz) at the corresponding field strength. This calculated value is only approximate since it is based upon a one-dimensional model in which the vibrationally excited state dipole moment is equal to the ground state value. A more complete analysis and careful calibration of the electric-field strength will be needed before quantitative comparisons can be made with the experimental spectra.

It is interesting to note that the intensities of the transitions fall off with increasing frequency shift from the band origin. This can be explained if one considers that the vibrational transition moment associated with this C-H stretch is along the axis of the trimer and that the degree of orientation with the field increases as you access states that are deeper in the potential. As noted above, the present geometry has the electric field of the laser perpendicular to that of the static field, which means that as the molecules become more highly oriented with the

applied field they are, on average, more orthogonal to the laser polarization direction, causing the transition intensities to decrease. Under these high-field conditions, the lowest-energy pendular state of the trimer has an rms deviation from the applied field direction, which to the authors' knowledge is the highest degree of orientation yet achieved in the gas phase for any system. The fact that these lowest pendular states become well resolved at high fields means that we can use laser probing techniques to both determine and precisely control the degree of orientation in these systems.

In the present study we have used high-resolution infrared spectroscopy to observe the onset of pendular behavior and have achieved an unprecedented degree of orientation. Work is presently under way to obtain complete assignments of the pendular states for both the trimer and the dimer of HCN. In this way, we will be able to quantify the degree of orientation that can be achieved in these systems. The apparatus is being modified so that even higher field strengths can be obtained and parallel polarization experiments can be carried out to more clearly observe the most highly oriented pendular states.

We wish to stress here that weakly bound molecular complexes may provide the key to studying steric effects for a wide range of molecules. The ability to form complexes containing the reagents of interest allows us to tailor the values of the dipole moment and rotational constant so that the pendular alignment technique can be used. On the other hand, the intermolecular interactions are so weak that, at least at high collision energies, they should not affect the chemistry of interest. Complexes may also be used to orient nonpolar molecules by simply forming a complex of the desired structure with a polar partner. The range of partners and resulting structures is so large that this should give a great deal of flexibility in achieving the desired orientation. Difficulties remain, however, such as how to eliminate the contributions to the chemistry from the largely unoriented monomer species present in the molecular beam. Nevertheless, the present study clearly shows that the pendular states of weakly bound complexes can provide us with a simple and completely general approach for achieving highly oriented species in a molecular beam.

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