

Near-infrared spectroscopy of ethylene and ethylene dimer in superfluid helium droplets

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The $\nu_5 + \nu_9$ spectra of ethylene, C_2H_4 , and its dimer, solvated in helium nanodroplets, have been recorded in the wavelength region near $1.6 \mu m$. The monomer transitions show homogeneous broadening of $\approx 0.5 \text{ cm}^{-1}$, which is interpreted as due to an upper state vibrational relaxation lifetime of $\approx 10 \text{ ps}$. Nearly resonant vibrational energy transfer ($\nu_5 + \nu_9 \rightarrow 2\nu_5$) is proposed as the relaxation pathway. The dimer gives a single unresolved absorption feature located 4 cm^{-1} to the red of the monomer band origin. The scaling of moments of inertia upon solvation in helium is 1.18 for the monomer and >2.5 for the dimer. In terms of the adiabatic following approximation, this classifies the monomer as a fast rotor and the dimer as a slow rotor. © 2005 American Institute of Physics. [DOI: 10.1063/1.1854630]

The spectroscopy of atoms and molecules solvated in (or attached to the surface of) helium nanodroplets is a rapidly advancing research field.¹ The rovibrational transitions in such spectra are, for the most part, quite sharp [$\leq 1 \text{ GHz}$ (Ref. 2)], suggesting coherence decay times on the order of 0.2 ns or longer.³ Typically, relaxation of populations is slower yet, going from tens of nanoseconds,^{4,5} to hundreds of microseconds⁶ when only deeply inelastic channels are open. Inelastic rotational relaxation with $\Delta E/hc \approx 5 \text{ cm}^{-1}$ is known to be fast (tens of picoseconds, as deduced by the much broader widths of the transitions⁶), because sufficient energy is available for both bulk roton creation and quantum evaporation.^{7,8} Otherwise, heavier rotors with lower excitation energies show much slower rates, and the corresponding lifetime broadening is often obscured by inhomogeneous broadening.^{5,9} Double resonance experiments performed on HCCCN (Refs. 4 and 5) and OCS (Ref. 10) suggest that couplings to surface excitations and to translational motion of the solute within the droplet allow for rotational relaxation.

Not only can rotational excitation energies be of the same magnitude as the energy of elementary excitations in helium, they can also be varied over more than two orders of magnitude by choice of the solute molecule. The existing literature provides examples of rotationally resolved spectra over a wide range of rotational constants, from which at least lower limits on relaxation times (as imposed by linewidths) can be deduced.² As yet, a quantitative theory of rotational relaxation of molecules in helium nanodroplets is still lacking.

Even more primitive is the state of our present knowledge of vibrational relaxation in helium nanodroplets. The observation (in virtually every case studied) of beam depletion upon vibrational excitation implies that vibrational relaxation occurs on time scales shorter than $100 \mu s$. Exceptions are HF and some of its complexes with rare gases, for which vibrational relaxation is found to be longer than, or comparable to, $100 \mu s$.^{6,11} The reason for this slow relaxation is the need to relax the entire vibration energy (3900 cm^{-1}) into hundreds of low-energy quanta of helium excitations and/or rotation and translation of the HF molecule. In simple models of collisional vibrational relaxation, such as that of Landau and Teller (see, e.g., Ref. 12) the relaxation probability falls exponentially with the exchanged energy.

For polyatomic molecules, faster vibrational relaxation in helium is observed, presumably due to the presence of vibration-to-vibration relaxation channels that allow much smaller quanta of vibrational energy to be transferred to the bath of helium excitations. This is consistent with what is known about vibrational relaxation in rare gases and liquids.¹³ As compared to rotational relaxation, vibrational relaxation data are harder to organize into a pattern because the rates are determined by many unrelated factors: (1) the need, in most cases, for many-quanta relaxation, (2) the weaker coupling of vibrational motion to the bath, and (3) the competition with intramolecular relaxation. The clearest information comes from those isolated cases where rovibrational transitions are abnormally broad: A linewidth significantly larger than one would expect based upon rotational relaxation alone suggests that vibrational relaxation also plays an important role. In some molecules, such as C_2H_2 (Ref. 14) and CH_4 (Ref. 15), purely rotational relaxation of certain transitions (in both the upper and the lower vibrational states) is simply not possible. States of different nuclear spin symmetry do not interconvert in helium on the time scale of present experiments^{3,4,14-17} and transitions be-

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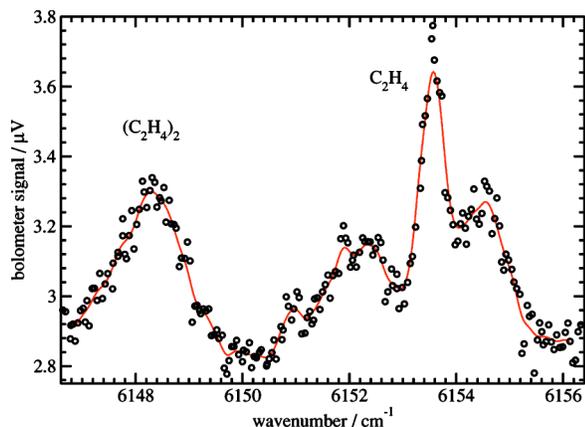


FIG. 1. Broad scan with assignment of the dimer (leftmost peak) and monomer (all other features) spectra. The line is a representation of the data smoothed with a Gaussian of FWHM of 0.24 cm^{-1} .

tween the lowest energy rotational state of a given symmetry in each vibrational state are possible. A strong dependence of the homogeneous broadening on the vibrational transition suggests that vibrational relaxation is playing an important role in at least one of the upper states.

In this work, we report on the $\nu_5 + \nu_9$ transition of ethylene (C_2H_4) and ethylene dimer in helium nanodroplets. This is a C–H stretch first overtone transition, near $1.6 \mu\text{m}$. It was previously studied in the isolated monomer by Platz and Demtröder.¹⁸ We observe the transitions through the depletion of the He droplet beam intensity they induce. The method and experimental apparatus have been previously described.³ The first spectroscopic study of ethylene in helium was performed by Behrens¹⁹ who used a line-tunable CO_2 laser to study the very strong ν_7 transition (see also the later work by Kunze *et al.*²⁰). However, because of the large spacing ($\approx 1 \text{ cm}^{-1}$) between laser lines, it cannot be excluded that transitions have been missed, and little information on the linewidth of the individual transitions can be extracted from the spectra. Following the present work, Lindsay and Miller¹⁷ measured the spectrum of ethylene in the $3 \mu\text{m}$ region, observing two C–H stretch normal modes: ν_{11} (parallel band, B_{1u} symmetry) and ν_9 (perpendicular band, B_{2u} symmetry). As will be demonstrated below, the much higher resolution observed for the ν_{11} fundamental greatly aided in the assignment of the present spectra. The present data and a preliminary analysis were previously presented in the Ph.D. thesis of one of the authors.²¹

Figure 1 shows the IR depletion spectrum we observed near 6150 cm^{-1} . Pressure dependence of the signal establishes that the transitions in the region $6150\text{--}6156 \text{ cm}^{-1}$ are due to the ethylene monomer and the broad peak, centered near 6148 cm^{-1} , is due to the dimer. Let us first analyze the monomer.

The contour of the monomer transition is clearly that of a parallel band, indicating that the upper state of the transition has B_{1u} vibrational symmetry. In line with what is normally observed in He droplets, we assume that the shift of the band center relative to that of the gas-phase molecule is at most a few cm^{-1} . This allows us to assign the transitions to the $\nu_5 + \nu_9$ combination band. The closest other B_{1u} state that

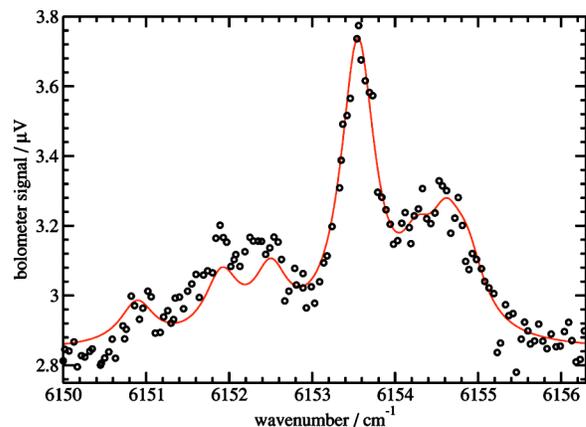


FIG. 2. Monomer portion of the spectrum and fit (see text).

has been observed in the IR spectrum of ethylene is centered at $6071.5755 \text{ cm}^{-1}$ and has been assigned to $\nu_1 + \nu_2 + \nu_{12}$.²² Because $\nu_5 + \nu_9$ is a parallel transition it should have the same rotational structure as the ν_{11} fundamental band observed by Lindsay and Miller.¹⁷ The ν_{11} band in helium consists of seven well resolved transitions spread over a range of 4.0 cm^{-1} and originating from the four populated levels $0_{00}, 1_{01}, 1_{11}, 1_{10}$, each being the lowest allowed state for a given nuclear spin symmetry. The ν_{11} spectrum is best fit assuming the above states have population ratios of 7:3:3:3, respectively, confirming that the populations of the nuclear spin states have not relaxed from their room temperature values.¹⁷ Given that the rotational structure is only partially resolved in our spectrum (unlike for the ν_{11} fundamental), we choose to fit our spectrum as a sum of seven Lorentzian lines with the same (fixed) integrated intensities and the same spacings (including the strong perturbation of $J=2$ levels) as observed in the ν_{11} band. In addition to the vertical offset and overall intensity scale factor, the band center, $\nu_0 = 6152.206(8) \text{ cm}^{-1}$, and the full width at half maximum of the lines, $\text{FWHM} = 0.52(2) \text{ cm}^{-1}$, are the only adjustable parameters of our fit. An alternative fit was done allowing each line to have an independently adjustable width, but did not significantly improve the agreement with the observed spectrum.

Figure 2 shows an expanded view of the observed $\nu_5 + \nu_9$ transition along with the fit. The band origin (taken as the midpoint between the two Q transitions) is blueshifted by $+1.2 \text{ cm}^{-1}$ from the gas-phase origin [$6151.00169(13) \text{ cm}^{-1}$] observed by Platz and Demtröder. This can be compared with a $+0.59 \text{ cm}^{-1}$ droplet-induced shift observed for the ν_{11} fundamental in He.¹⁷

The FWHM of the $\nu_5 + \nu_9$ transitions, $0.52(2) \text{ cm}^{-1}$, is more than one order of magnitude larger than the corresponding lines in the ν_{11} band. This suggests that rotational relaxation of the lower state of each transition, as well as inhomogeneous broadening should make minor contributions to this value. If we assign the entire width as due to lifetime broadening of the upper state of each transition, we can deduce that the excited vibrational state has a lifetime of $\sim 10 \text{ ps}$, remarkably similar to what Lindsay and Miller observed for the ν_9 transition of C_2H_4 (asymmetric C–H stretch fundamental) at about 3110 cm^{-1} .

To justify this fast relaxation as vibrational, we have to find a candidate pathway. For this purpose it is better to move from a normal- to a local-mode picture: previous studies²³ have indeed shown that the region of the first C–H stretching overtone is intermediate between a local- and a normal-mode description. $\nu_5 + \nu_9$ is the highest of the four possible B_{1u} symmetric normal mode states with two quanta of C–H stretch; there exist Darling–Dennison coupling terms that will mix all of these four normal mode states.²² If one looks at the combination of the normal mode displacements for the sum of ν_5 and ν_9 , one gets an antisymmetric CH_2 stretch ($a\text{-CH}_2$) localized on one end of the molecule.²² The $\nu_5 + \nu_9$ state can thus be described as the u -symmetry combination of two $a\text{-CH}_2$ overtones localized on each end of the molecule. One can expect that nearly isoenergetic will be a g -symmetry combination of the same $a\text{-CH}_2$ stretches. In the Raman spectrum of ethylene, Knippers *et al.* have observed a transition at 6138 cm^{-1} which they assign as $2\nu_5$ (Ref. 24) that could also be described as just the above local-mode combination. In the gas phase, this state is only 13 cm^{-1} below the $\nu_5 + \nu_9$ state, and relaxation between the two states can proceed by emission of a single quantum of helium excitation (phonon/roton) so long as the latter has an antisymmetric character (since this will break the g/u symmetry of the molecular environment).

We now turn to the spectrum of the ethylene dimer. In the gas phase, the complex has been shown by Chan *et al.*²⁵ to have a D_{2d} structure with two equivalent monomers whose molecular planes intersect at right angles. While it is possible that the structure of the dimer formed in helium droplets be different, we will analyze the unresolved dimer band near 6148 cm^{-1} assuming the gas-phase structure. We note that long range forces, rather than thermodynamic equilibrium, may determine the structure of complexes formed in He droplets^{26,27} and that the D_{2d} structure has a favorable quadrupole-quadrupole interaction.

We do not expect dimerization to induce a large band shift relative to the separation of different bands observed in the gas phase. Given the small shift of the dimer band from the monomer $\nu_5 + \nu_9$ transition, we assign the dimer transition to the same $\nu_5 + \nu_9$ excitation, delocalized over each monomer unit; this leads to a perpendicular transition in the dimer.

Because this particular transition has never been observed for the gas-phase complex, assessment of the droplet-induced shift is not possible. The small shift from the corresponding monomer transition ($\approx -4\text{ cm}^{-1}$) suggests that the vibrational motions are very weakly perturbed by formation of the dimer, a fact which corroborates the assumed gas-phase D_{2d} structure, since in this case the vibrational dipole moments are perpendicular to the intermolecular separation.

From the unresolved envelope we can extract some information on the rotational constants: for this purpose the rotational structure of the dimer spectrum was simulated as that of a perpendicular transition in a rigid symmetric top. The ground state rotational constants were taken from Chan *et al.*,²⁵ and the change upon vibrational excitation was assumed to be twice that observed for the C–H fundamental. These rotational constants were scaled by an adjustable fac-

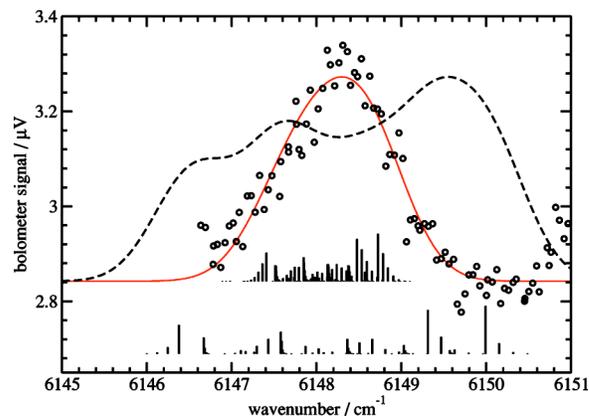


FIG. 3. Dimer portion of the spectrum in Fig. 1 (circles) along with two simulations [dashed line, unscaled gas-phase rotational constants ($\kappa=1$); continuous line, scaled rotational constants ($\kappa=0.31$); sticks, simulated spectra before convolution]. In each case, the other parameters of the simulation are least squares fit to the spectrum.

tor κ to account for the well-known reduction, in helium, of the rotational constants of molecules from their gas-phase values.² The temperature was assumed to be 0.38 K and the spin weights were taken from Chan *et al.* and assumed not to interconvert in helium. The calculated “stick spectrum” was convoluted with a Lorentzian line shape with a single FWHM which was also a fit parameter, along with the shift of the spectrum, an intensity scale factor, and an offset. The fit only included the portion of the spectrum with wave number less than 6150.5 cm^{-1} , due to overlap with the monomer above this value. The resulting best fit is compared with the observed dimer spectrum in Fig. 3. The best fit values are $\kappa=0.31$, $\nu_0=6148:10\text{ cm}^{-1}$, and the FWHM of the lines $=0.99\text{ cm}^{-1}$ (implying an excited state lifetime of 5 ps). Plots of the fit χ^2 as a function of κ (with other parameters optimized at each point) indicate that the statistical 2σ confidence interval for κ is $[0.22, 0.36]$. The fit to the spectrum is substantially worse for $\kappa > 0.4$, i.e., the effective moment of inertia for rotation of the dimer in helium is at least a factor of 2.5 times larger than for the corresponding rotation in the gas phase. Values of κ less than the optimal value can be accommodated by increasing the broadening parameter. This limit on the value of κ is consistent with the fact that the rotational constants of most heavy rotors in helium are reduced by a factor of ≈ 3 from their corresponding gas-phase values.² If one interprets the increased moments of inertia in terms of an adiabatic dragging of helium density with the rotation, based on geometry arguments alone one would expect the fractional increase in the moment of inertia I_A , for the dimer to be smaller or at most the same as that of the moment of inertia I_B for the monomer. The latter is, however, only $+18\%$.¹⁷ The large discrepancy between monomer and dimer inertia most likely reflects the breakdown of the adiabatic following approximation²⁸ for the fast rotational motion of the C_2H_4 monomer. The threshold value of the rotational constant between slow and fast rotors is traditionally set at $\sim 1\text{ cm}^{-1}$.²

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