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Contaminated torsional tunneling splittings in five normal-mode vibrations of propene

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Sub-Doppler infrared spectra of five normal-mode vibrations of propene between 900–1100 cm^{-1} reveal strongly perturbed torsional tunneling splittings due to nonresonant anharmonic couplings to vibrational states in which the torsional mode is excited. The present results suggest that perturbed tunneling splittings will be a general feature for vibrationally excited states. Consequently, care should be taken when using tunneling splittings to obtain the vibrational dependence of a tunneling barrier. Instead, tunneling splittings in excited states can be used as a probe of long-range vibrational–torsional state mixing in molecules.

The investigation of the coupling between large- and small-amplitude vibrations has attracted recent interest^{1,2} due to the possible role of large-amplitude motions in promoting intramolecular vibrational energy redistribution (IVR). These interactions are also important in other dynamical processes such as vibrational predissociation of weakly bound complexes³ and infrared-induced conformational interchange in molecules trapped in rare-gas matrices.⁴ A direct measure of the coupling of internal rotation or inversion motions and small-amplitude vibrations can be obtained by measuring the vibrational dependence of the barrier to tunneling. Typically, barriers are inferred by fitting the measured tunneling splitting in a vibrational state to an assumed form of the large-amplitude potential. This approach assumes the validity of an adiabatic separation of the large- and small-amplitude vibrations so that a large-amplitude potential surface can be defined.

Recent analysis of internal-rotation or inversion splittings in the high-resolution infrared spectra of the C–O^{5–7} and O–H⁸ stretches in methanol, a C–H stretch in ethane,⁹ the CH₃ rocking vibrations in ethane,^{10,11} CH₃SiH₃,¹² and CF₃CH₃,¹³ and the C–C stretch¹⁴ and a torsional combination band¹⁵ in acetaldehyde, and the N–H fundamental¹⁶ overtone vibrations of HN₃,¹⁷ suggests that tunneling splittings measured in vibrationally excited states will not give direct information on barrier changes. These tunneling splittings are likely to have contributions from resonant and nonresonant anharmonic and Coriolis coupling to combination vibrations which have a high degree of excitation in the large-amplitude mode. To investigate the generality of tunneling splittings being perturbed by anharmonic interactions we have measured the infrared spectra of five normal-mode vibrations of propene (CH₃CH=CH₂) in the 900–1100 cm^{-1} region. Spectra were recorded using a 2 MHz resolution tunable microwave-sideband CO₂/N₂O laser electric-resonance optothermal spectrometer (EROS).^{18,19} For each normal mode we have determined the $J=0$ A – E tunneling splittings associated with the large-amplitude –CH₃ internal rotation. For $J=0$, the change in tunneling splittings from the ground-state value must arise either through a vibrational dependence of the barrier to internal rotation, a

change in the reduced mass for internal rotation, or anharmonic interactions with other vibrational states.

The microwave^{20,21} and low-resolution infrared²² spectra of propene have been well characterized. Our combined analysis of the microwave spectrum of the ground torsional state²¹ together with the far-infrared spectrum,²³ using a program described previously,²⁴ gives a ground-state A/E torsional splitting of 101.9 MHz and a torsional barrier of 708.4 cm^{-1} . The torsional tunneling splits the microwave transitions into well-resolved A and E symmetry components, allowing microwave-infrared double-resonance assignment of the A and E symmetries of the infrared transitions. Because of the small magnitude of the torsional splittings compared to the rotational constants, the infrared band structure of propene qualitatively resembles that of an asymmetric top in which each transition is split into a doublet by the internal rotation. A sample spectrum showing a section of the ν_{13} and ν_{19} bands obtained using the EROS instrument is given in Fig. 1. The sign and magnitude of the signals are a function of the usual transition moment and Boltzmann factors, as well as the differential focusing characteristics of the upper and lower states of the transitions in the electric quadrupole state selector.²⁵

In Table I we summarize the results of the present investigation. Listed are the vibrations studied, their symmetries in the C_s point group, the observed band types, the E state and A state $J=0 \leftarrow 0$ band origins, and the A – E tunneling splittings. For comparison, the ground-state tunneling splitting is also given. The A'/A'' symmetries found in the low-resolution studies²² are consistent with the band types observed in the present study. The $J=0$ origins were determined by direct measurements of the energy-level position of the vibrationally excited $J=0$ states relative to the A or E ground $J=0$ state. In cases where the limited sideband coverage prevented direct access of an excited $J'=0$ state, microwave-infrared double-resonance was used to probe the $J'=0$ upper state. The absolute band origins presented in the table are estimated to be accurate to better than 2 MHz, limited by our knowledge of the exact Doppler shift arising from the nonorthogonal crossing of the laser and molecular beams. The precision of measurements

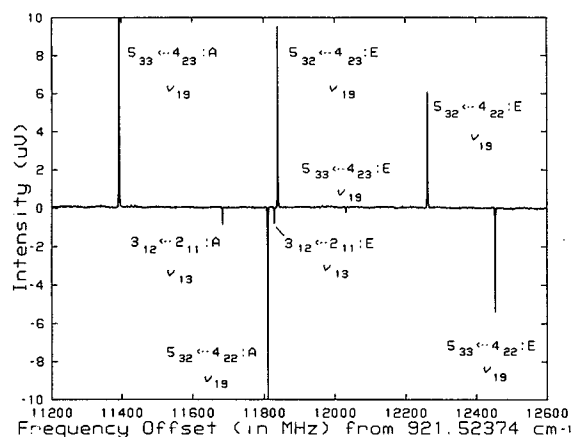


FIG. 1. N_2O -laser sideband spectrum of propene showing overlapping transitions from the ν_{13} and ν_{19} bands. The spectrum was recorded with the laser operating on the $P(20)$ line of the $10\ \mu\text{m}$ band of N_2O using a time constant of 125 ms while stepping the microwave frequency synthesizer in 500 kHz steps. All the labeled transitions are observed on the negative sideband of the laser. Note for the c -type ν_{19} band the presence of forbidden b -type transitions for the E state which are allowed by the internal rotation. Because of the effects of the state focusing these transitions appear stronger than some of the allowed transitions.

made within the same vibrational band is $\sim 0.25\ \text{MHz}$ (1σ), which is nearly an order of magnitude smaller than the $2\ \text{MHz}$ (FWHM) linewidth. For two of the bands, ν_{17} and ν_{19} , transitions to perturbing states were observed. The complete band assignments will be given in a later publication.

As seen in the table, the A/E tunneling splittings vary significantly between the bands. For three of the vibrations the tunneling splittings have changed sign from the ground-state value. Such a sign change cannot be achieved by adjusting the height of the internal-rotation barrier from the ground-state value, and must be due to anharmonic coupling of the normal-mode vibrations to background vibrational states. Most likely the coupling is dominated by one or more bath states having an odd number of quanta in the torsional coordinate. Such a state will have its A state above its E state, opposite to that observed in the ground state, forcing the tunneling splitting of the normal-mode

TABLE I. Observed A (ν_A^A) and E (ν_E^A) $J=0\leftarrow 0$ band origins, band types and $E-A$ tunneling splittings (ν_t) for five normal modes of propene.

Vibration	Symmetry	Band type	ν_E^A (cm^{-1})	ν_A^A (cm^{-1})	ν_t (MHz)
Ground state	A'	a/b	0.000 00	0.000 00	+101.9
ν_{12}	A'	a/b	935.673 79	935.677 99	-23.8
ν_{13}	A'	a/b	919.293 42	919.299 76	-87.9
ν_{17}	A''	c	1045.192 20	1045.207 05	-343.3
ν_{18}	A''	c	990.778 29	990.775 38	+189.1
ν_{19}	A''	c	912.672 63	912.666 74	+279.7

^a ν_A^A and ν_E^A are the frequencies for the hypothetical $J=0\leftarrow 0$ transitions for the A and E symmetry species, respectively.

^bThe absolute band origins are estimated to be accurate to $\pm 2\ \text{MHz}$.

^cThe uncertainties on ν_t for the excited vibrational states are $\sim \pm 0.4\ \text{MHz}$.

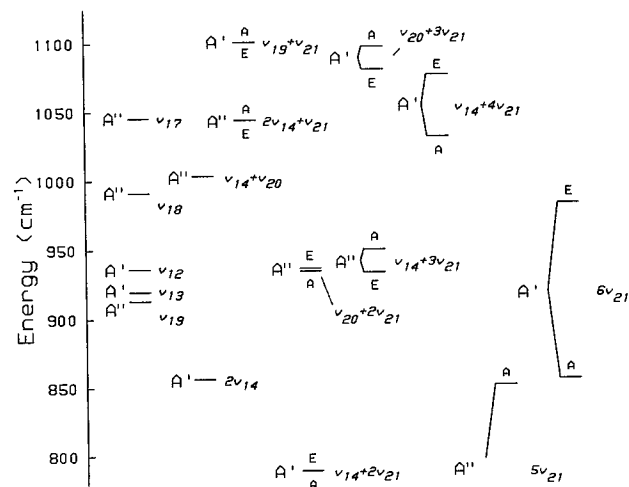


FIG. 2. Energy-level diagram for propene showing the five normal modes studied and the background vibrational states. The background states are presented from left to right in order of increasing number of quanta in the torsional state.

vibration to be reduced or even change sign. Coupling to states with an even number of quanta in the torsional coordinate can also decrease or invert the tunneling splitting of the normal-mode state if the E component of the background state lies above the normal-mode state and the A component lies below.

For the ν_{18} and ν_{19} normal modes the tunneling splittings have increased from the ground-state value. This increase could indicate that the V_3 torsional barrier has decreased in the excited vibrational state. To assess this possibility we have calculated the change in the V_3 barrier from the ground-state value of $708.4\ \text{cm}^{-1}$ necessary to give the observed ν_{18} and ν_{19} tunneling splittings. For ν_{18} , the barrier must decrease by $73\ \text{cm}^{-1}$ and for ν_{19} , the barrier must decrease by $117\ \text{cm}^{-1}$. Such large barrier changes ($> 10\%$) appear unrealistic. For comparison, the change in zero-point structure of propene in $\text{CH}_3\text{CD}=\text{CH}_2$ and *trans*- $\text{CH}_3\text{CH}=\text{CHD}$ affects the V_3 barrier by less than 1% . These large barrier decreases, when combined with our observation of three reversed A/E splittings for the other bands, are most likely attributed to the presence of anharmonic couplings to states in which the torsional mode is excited. In this case the coupling is likely to be dominated by a state or states with an even number of torsional quanta to ensure that the A/E energy-level ordering stays the same as in the ground state. Analogous to the negative tunneling splitting case, a state with an odd number of quanta in the torsional coordinate can also increase the A/E splittings for the normal-mode state if the normal-mode state falls between the two tunneling components of the perturbing state.

In Fig. 2 we draw a vibration-torsion energy-level diagram for propene in the region between 800 and $1100\ \text{cm}^{-1}$. Shown are the normal-mode vibrations studied and the various background vibrational states which can couple to the normal-mode states. The background states are ordered from left to right by the number of quanta in the

TABLE II. Anharmonic matrix elements (cm^{-1}) required to account for the measured E - A tunneling splittings assuming a two-state interaction.^a

Bath state ^b	ν_{12} (A')	ν_{13} (A')	ν_{17} (A'')	ν_{18} (A'')	ν_{19} (A'')
$\nu_{19} + \nu_{21}$ (A')	30.43	40.95			
$\nu_{14} + 2\nu_{21}$ (A')					
$\nu_{20} + 3\nu_{21}$ (A')	2.41	3.28			
$\nu_{14} + 4\nu_{21}$ (A')					
$6\nu_{21}$ (A')	0.35	0.45			
$2\nu_{14} + \nu_{21}$ (A'')			0.41		
$\nu_{20} + 2\nu_{21}$ (A'')				2.11	1.23
$\nu_{14} + 3\nu_{21}$ (A'')			3.07		
$5\nu_{21}$ (A'')			2.83		

^aThe shift of the bright-state energy level in second-order perturbation theory is given by: $\text{shift} = W^2/(E_b - E_d)$, where W is the coupling matrix element, E_b is the unperturbed bright-state energy, and E_d is the unperturbed dark-state energy.

^bThe methyl torsion is denoted by ν_{21} and the positions of the "overtone" are calculated using the reported ground-state V_3 and V_6 terms. There are only two other low-lying normal modes for propene: ν_{14} (A') at 428 cm^{-1} and ν_{20} (A'') at 575 cm^{-1} (Ref. 21). These normal modes are treated as harmonic in the calculation of the combination and overtone frequencies.

torsional coordinate. Torsional frequencies for each vibrational state were estimated using the Hamiltonian $H = F\mathbf{p}^2 + V_3(1 - \cos 3\alpha)/2 + V_6(1 - \cos 6\alpha)/2$, and the ground-state values of $V_3 = 708.4 \text{ cm}^{-1}$ and $V_6 = -21.7 \text{ cm}^{-1}$. Here, α is the internal rotation angle, \mathbf{p} is its conjugate angular momentum, and $F \equiv \hbar^2/2I_\alpha = 7.133 \text{ cm}^{-1}$ as determined from our internal rotation fit of the microwave and far-infrared data. The I_α term in F is the reduced moment of inertia for internal rotation of the methyl top. The anharmonic selection rules in C_s are $A' \leftrightarrow A'$ and $A'' \leftrightarrow A''$ for the vibrational coupling. For the E symmetry states this selection rule is not rigorous, except in the infinite barrier limit. As a result, the "forbidden" $A' \leftrightarrow A''$ anharmonic couplings in the E symmetry states become stronger with increasing excitation of the internal-rotation motion.

Table II presents estimated anharmonic matrix elements between the normal-mode vibrations and the various background states necessary to produce the observed perturbed tunneling splittings. The assumption is made that the change in the normal-mode tunneling splitting from the ground-state value is dominated by coupling to a single background state. We take the coupling matrix elements to be the same for the A and E tunneling components. In reality, the observed changes in tunneling splittings arise from the sum of contributions from the coupling of the normal-mode vibration to all the bath states of the correct symmetry. The torsional splittings thus provide a measure of the asymmetry of the vibrational bath in the large-amplitude coupling. As seen in the table, the smallest values for the matrix elements necessary to account for the perturbed tunneling splittings in each state vary from 0.35 to 2.11 cm^{-1} . These coupling strengths lie within the range of torsional-vibration matrix elements determined for vibrations in CF_3CH_3 ,¹³ 2-fluoroethanol ($\text{CH}_3\text{FCH}_2\text{OH}$),²⁶ and acetaldehyde.²⁷ In those molecules torsional-vibration matrix elements of 21 , 0.7 , and 0.1 cm^{-1} are found to

interchange 3 , 4 (or 5), and 6 vibrational/torsional quanta, respectively.

At higher energies the effective tunneling splittings might be expected to take on values characteristic of the unperturbed vibration as the asymmetry in the large-amplitude coupling gets reduced due to averaging among the large number of background states. The observation of this trend is complicated by the onset of intramolecular vibrational energy redistribution (IVR) at higher energies. In an IVR regime, the A and E symmetry transition states are each split into a number of components by near-resonant coupling of the normal-mode state to the large density of nearby states consisting of overtones and combination vibrations of lower frequency normal modes. The width of these two IVR multiplets will generally overlap making it difficult to assign the symmetry of an individual line. Microwave-infrared or infrared-infrared double-resonance allows the assignments of the tunneling symmetries of the transitions. In the case of amine hydrogen interchange tunneling in the acetylenic C-H stretch vibration of propargyl amine ($\text{HC}\equiv\text{CCH}_2\text{NH}_2$), where the IVR widths of the symmetric and antisymmetric states overlap, double-resonance results show that the corrected line centers for the symmetric and antisymmetric transitions do not coincide.²⁸ Assignment procedures of highly perturbed spectra that are based on requiring coincident line centers for different torsional species^{29,30} can be subject to error when bath asymmetry effects are still present.

Other spectroscopic observables could, in principle, be used to investigate coupling to excited large-amplitude states. For example, vibrational mode coupling can lead to perturbed rotational constants. In propyne, nonresonant vibrational mode coupling results in anomalous K -subband origin spacings.³¹ Unlike the $J=0$ tunneling splittings, rotational perturbations are affected by both Coriolis and anharmonic interactions. Moreover, due to the difficulty of estimating values of the unperturbed rotational constants, it is generally not straightforward to determine whether the rotational constants are contaminated. Intensity transfer from the infrared allowed vibrational band to the perturbing state(s) is a traditional measure of mode coupling, however for nonresonant couplings, such as observed in propene, the perturbing state typically does not gain sufficient intensity to be observed. In contrast to other tests of mode mixing, torsional splitting are most sensitive to very high-order couplings since the larger the tunneling splitting of the perturbing state the smaller the matrix element required to affect the torsional splittings of the normal mode to the same extent.

In summary, we have shown that the tunneling splitting in the normal-mode vibrations of propene are contaminated by nonresonant coupling to a subset of bath states having the torsional mode excited. This contamination makes it difficult to use tunneling splittings to estimate barriers in excited vibrational states to extract information about the coupling of high-frequency modes to the large-amplitude coordinate. Instead, the tunneling splittings furnish a sensitive probe of the couplings to the vibrational bath. Extension of the *ab initio* methods used by Gaw

*et al.*³² to model spectroscopic constants in small molecules to systems with internal rotation system may allow quantitative information to be obtained about the couplings to the large-amplitude bath.

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