Journal of Molecular Spectroscopy 270 (2011) 123–131

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Reexamination of the $C_2H_3^+$ microwave and infrared spectra

Jon T. Hougen [a],*, Laurent H. Coudert [b]

[a] Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441, USA
[b] LISA, UMR 7583, CNRS, Universités Paris 12 et Paris 7, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

ARTICLE INFO

Article history:
Received 17 August 2011
In revised form 16 September 2011
Available online 29 September 2011

Keywords:
$C_2H_3^+$
Barrier height
Hydrogen migration
Protonated acetylene
Rotational spectrum
Tunneling splittings
Vibrational spectrum

ABSTRACT

The high-resolution infrared spectrum of $C_2H_3^+$ recorded in the 3μ CH stretching region (J. Phys. Chem. 99 (1995) 15611–15623) is re-analyzed using an effective internal axis method (IAM) Hamiltonian to account for tunneling splittings associated with the large amplitude hydrogen migration motion. The line position analysis carried out with this approach allows us to fit 63% of the data with a standard deviation of 0.05 cm^{-1}, using eight parameters, including the band center, five semi-rigid-rotor spectroscopic constants, and two parameters describing the magnitude of the tunneling splitting and its rotational dependence. The rotational dependence of the observed tunneling splittings is described by an angular offset θ, which can also be calculated theoretically from *ab initio* equilibrium and transition-state structures already in the literature. The agreement between fitted and calculated values of θ, as well as agreement with the value determined from a previous treatment of splittings in the vibrational ground state, gives strong support for the validity of the model. Additional support is provided by the barrier height of 1488 cm^{-1} determined here from the ground state splittings, which agrees well with an *ab initio* estimate of 1300 ± 450 cm^{-1}. The principal problem in the present treatment of the infrared data is the fact that observed minus calculated residuals for 37% of the assigned lines are greater than 0.05 cm^{-1}. This is believed to be due to random perturbations by dark states.

1. Introduction

Although the 3μ infrared spectrum [1,2] and the sub-millimeter-wave spectrum [3,4] of the vibrational ground state of protonated acetylene $C_2H_3^+$ were observed and analyzed some time ago, with help from a variety of theoretical papers [5–10] stimulated by these observations, unanswered questions concerning the hydrogen migration motion in this ion remain. In this paper we revisit the treatment of tunneling splittings associated with this large-amplitude motion (LAM) using an existing high-barrier tunneling Hamiltonian [9,10], in an attempt to evaluate that Hamiltonian's level of success for the ground and one fundamental vibrational state of $C_2H_3^+$, and to suggest new experimental measurements which could increase our knowledge of the $C_2H_3^+$ energy levels and the hydrogen migration motion.

The LAM of interest here is one in which the three H atoms rotate around the C–C core. Pictorial representations of this LAM can be found in Fig. 2 of Ref. [5] and Fig. 1 of Ref. [9], both of which reflect two theoretical assumptions on the hydrogen trajectories, namely that: (i) all five atoms remain in a plane during the LAM, and (ii) the H atoms do not overtake each other. Fig. 3 of Ref. [9] indicates that this LAM can be topologically reduced, for simplicity of classical mechanical, quantum mechanical, and permutation-inversion group theoretical thought, to the internal rotation of an equilateral triangle of H atoms about a stick connecting the two C atoms.

Theoretical discussions in the literature can be divided into two groups. The ground-state sub-mm measurements were first understood qualitatively and explained semi-quantitatively by theoretical works [5–8] based on solving the large-amplitude migration-rotation problem on an *ab initio* potential surface, which turned out to have six equivalent potential minima separated by relatively high potential barriers. In particular, Ref. [6] presents the minimum energy path from the classical to the non-classical configuration, as calculated by several *ab initio* methods, under the assumption that the molecule remains planar along the path. Ref. [7] then uses the CAS SCF path determined in Ref. [6] to predict, without experimental input, the rotational energy levels and internal-rotation tunneling splittings expected in the ground vibrational state.

Solving Schrödinger's equation for motion on a potential surface is certainly the method of choice in principle, but computational limitations often prevent prediction of spectral line positions with residuals comparable to experimental measurement precision. We thus focus here on a phenomenological high-barrier tunneling Hamiltonian method [9–12], summarized briefly in Section 2, which does not require explicit knowledge of the potential energy surface, but which is often capable of spectral fits to experimental accuracy. It should be noted, however, that such a phenomenological

---

* Corresponding author. Fax: +1 301 975 2950.
E-mail address: jon.hougen@nist.gov (J.T. Hougen).

0022-2852/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2011.09.005

Hamiltonian, in contrast to the methods [5–8] described in the preceding paragraph, has no predictive power until its parameters have been determined by a least squares fit of some set of measured and assigned experimental data. Furthermore, the phenomenological Hamiltonian [9–12] used here will only work well for an isolated vibrational state, i.e., a state not suffering from external perturbations.

Although historically the infrared work preceded the sub-millimeter work, we discuss the experimental data in Sections 3 and 4 in the opposite order, to facilitate understanding of the theoretical questions that arise.

2. Brief summary of the high-barrier tunneling formalism

As a simple analogy, consider two ways of treating the rotational levels of a semi-rigid polyatomic molecule: (i) one can diagonalize a matrix containing parameterized matrix elements derived from an effective rotational Hamiltonian with terms of the form $AJ_z^2 + BJ_x^2 + CJ_y^2 - D_J J^4 + \cdots$, or (ii) one can numerically solve Schrödinger's equation for the vibrational and rotational energy levels associated with a calculated *ab initio* potential energy surface. The high-barrier tunneling formalism [11,12] is analogous to (i).

Matrix elements of the one-dimensional tunneling Hamiltonian formalism used here depend on two main parameters. The first parameter involves a relatively familiar concept, since it represents the nearest-neighbor tunneling frequency h in the non-rotating molecule, which corresponds for $C_2H_3^+$ to the frequency of tunneling between an adjacent pair of the six equivalent minima that can be drawn for the approximately T-shaped non-classical equilibrium structure [1,6]. The other parameter is an "angular offset" θ, which is much less familiar and is described in more detail below. This parameter controls (to first order) the J and K variation of the tunneling splittings in the rotating molecule through its appearance in a Wigner $D^J(0,\theta,0)_{KK}$ function, which leads to a damped-oscillation behavior for the tunneling splittings when they are plotted against J for given K.

We stress again that the tunneling model above does not need a potential surface as input and does not return a potential surface as output. All details of the multidimensional potential surface of the molecule that are important for the tunneling motion considered (and its associated tunneling splittings) are replaced in this phenomenological Hamiltonian by the two parameters mentioned above, together with some small J and K centrifugal distortion corrections to these terms.

The appearance of the angular offset θ can be understood relatively easily by spectroscopists familiar with the expression for high-barrier internal-rotation tunneling contributions to energy levels in a near-symmetric top molecule with a methyl top nearly coaxial with the principal rotational a axis (e.g., methanol). As is well known [13], the K-dependence of those tunneling splittings can be represented for A-species levels ($\sigma = 0$) and E-species levels ($\sigma = \pm 1$) by a Fourier series of the form

$$E = F \sum_n a_n \cos[(2\pi n/3)(\rho K - \sigma)], \tag{1}$$

The angle θ in the present formalism is the analog of the quantity $(2\pi/3)\rho$ in the $n = 1$ term of Eq. (1) [14]. This analogy is not perfect, however, since the first term of Eq. (1) gives rise to undamped oscillations in K which are independent of J. Although not discussed in detail here, this imperfect analogy arises mathematically from the fact that hydrogen migration in $C_2H_3^+$ generates angular momentum about the c axis, so that θ appears in the second position in the argument list of the Wigner function $D^J(0,\theta,0)_{KK}$, whereas internal rotation in methanol generates angular momentum about the a axis, so that θ appears in the first position $D^J(\theta,0,0)_{KK}$.

The origin of the angular offset in $C_2H_3^+$, which represents the amount that the whole molecule must be rotated backwards about the c axis to cancel out the angular momentum generated by one step of the hydrogen migration motion, can be described pictorially [9,14] as follows. Let the molecule-fixed axis system for the $C_2H_3^+$ molecule in each of its six minima be chosen with the z axis parallel to the C$\equiv$C bond and the y axis perpendicular to the plane of the molecule. The H migration motion then generates, as the molecule moves from one minimum to the next, an angular momentum perpendicular to the molecular plane (i.e., along the c inertial axis) in the molecule-fixed axis system. This angular momentum has a value of $I_{H3} \times 2\pi/6$, where I_{H3} is some average moment of inertia of the H_3 "triangle" [9] during its "rotation" around the C$\equiv$C bond. But traditional vibration–rotation theory tells us [15] that large and troublesome first-order energy contributions of Coriolis interactions are removed only in the Eckart axis system, in which there is no residual vibrational angular momentum (to first order). To change to an Eckart system representation in the present case, the angular momentum generated by the H_3 rotation must be canceled by rotating the whole molecule backwards by an angle $\theta = (2\pi/6) \times [I_{H3}/I_{mol}]$, where I_{mol} is the moment of inertia of the whole molecule about its (out-of-plane) $y = c$ axis.

As a result of requiring the molecule to be in an Eckart axis system during its tunneling motion, e.g., as a result of simultaneously rotating the whole molecule backwards in the molecule-fixed axis system during the tunneling motion from minimum 1 to minimum 2, the C$\equiv$C bond will no longer be parallel to the z axis when the molecule and its associated rotational wavefunction from minimum 1 reach the position of minimum 2. But when the $1 \to 2$ tunneling matrix element (or for conceptual simplicity, the $\langle J,K_{a1},K_{c1}|J,K_{a2},K_{c2}\rangle$ overlap integral) is calculated mathematically, all rotational functions must be expressed in the same coordinate system before integrating. Clearly, since the rotational wavefunction from minimum 2 still has its C$\equiv$C bond parallel to the z axis, while the rotational wavefunction that "travelled" to minimum 2 from minimum 1 does not, there is some angular offset in the orientation of the two molecule-fixed axis systems. This angular offset is equivalent for the present $C_2H_3^+$ problem to a rotation about the y axis through the angle θ.

For further qualitative understanding, we note that the angular offset θ plays essentially the same mathematical role in this rotational problem as the internuclear distance offset Δr_e plays when calculating diatomic $\langle v'|v''\rangle$ Franck–Condon factors for electronic transitions between two potential curves with different equilibrium bond lengths. We can thus loosely refer to tunneling integrals of the type $\langle J,K_{a1},K_{c1}|J,K_{a2},K_{c2}\rangle$ as rotational Franck–Condon factors. For more information on the mathematical details associated with the rotational offset θ, the reader is referred to Refs. [9,11,12].

3. Ground-state millimeter-wave measurements and fit

Tables 3 and 4 of Ref. [10] show the presently existing 20 submm-wave measurements in the vibrational ground state of $C_2H_3^+$, together with observed-minus-calculated residuals from a least-squares fit to seven S-reduction rotational constants (A, B, C, D_{JK}, D_J, d_1, and d_2) and the two tunneling splitting parameters (h, θ) mentioned above. The fit is excellent, so from one point of view there is nothing more to be done. From another point of view, however, that successful fit cannot be taken as an unequivocal demonstration of the success of the present phenomenological Hamiltonian tunneling formalism for treating H migration motion, because only three observed splittings are fit to two splitting parameters [10].

Even though the present formalism has been successfully applied to a number of other molecules with a variety of LAM