An Algebraic Approach for Determining the Vibrational Spectroscopy and Potential Energy Surface of the Quasi-Linear Tetratomic Molecule HCNO

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A potential energy surface and the vibration spectroscopy for the nonlinear tetratomic molecule HCNO are obtained using the U(4) group. This potential energy surface includes the bending motion information. In addition some properties, including the dissociation energy, force constant, and saddle points, are discussed.

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I. INTRODUCTION

It is well known that HCNO is a complex family of structural isomers which has attracted considerable attention [1, 2]. The interest here lies in its identification as “the most distinctly quasilinear... among the HXYZ molecules.” The concept of quasi-linearity was introduced to describe polyatomic molecules having a bending potential function with a medium-sized quartic component about linearity, giving either a linear equilibrium geometry with a flat-bottomed nonparabolic potential or a nonlinear equilibrium geometry with a small barrier to linearity. Semicrystal fitting of experimental HCNO data to the semirigid bender model for rovibrational dynamics has suggested no significant barrier to linearity. So we can take the molecule as having quasi-linearity.

Some investigators [1, 2] have made a number of studies on HCNO. Recently, one obtained a large amount of spectroscopic data of the molecule [3]. Information about the potential energy surfaces has improved enormously in recent years, both from the analysis of experimental data and from ab initio calculations, but it is still a major task to gather this information into a functional representation which can be used for calculations.

The success of the interacting boson model of Arima and Iachello [4] has stimulated new interest in the study of many-body systems governed by an algebraic Hamiltonian. In particular the properties of Hamiltonians with U(4) as the dynamical symmetry group have been investigated by several groups. It has been shown that algebraic techniques are a powerful tool for the description of both time independent and time dependent phenomena [5–9].

Recently, the algebraic approach has been shown to be capable of providing an accurate description of the highly excited state spectra of linear tetratomic molecules and their potential energy surface. Few have obtained the potential energy surface of nonlin-
ear tetramolecular molecules. In this paper, we derive the vibration spectroscopic data and the potential energy surface of the quasi-linear tetramolecular molecule HCNO using the U(4) algebra, and obtain the potential energy surface including the bond angle information.

II. BRIEF DESCRIPTION OF THE THEORY

At the beginning of the 2000s, several authors used the algebraic U(4) model to discuss molecular spectra. The papers dealing with triatomic molecules [9–12] treated tetramolecular molecules using the same method. An extensive discussion of linear tetramolecular molecules within the framework of the U(4) model is given in Ref. [13]. The detailed procedure for deriving the potential energy surface of linear tetramolecular molecules by using the Lie algebraic approach is shown in Refs. [14, 15]. We do not repeat it here, but only emphasize the main points.

For tetramolecular molecules, the dynamical symmetric group chain is

\[ U_1(4) \otimes U_2(4) \otimes U_3(4) \supset SO_1(4) \otimes SO_2(4) \otimes SO_3(4) \supset SO_{12}(4) \otimes SO_3(4) \supset SO_{123}(4) \supset SO_{123}(3) \supset SO_{123}(2). \]

So the Hamiltonian of tetramolecular molecules can be written as a combination of the Casimir operators of the subgroup chain \( U_1(4) \otimes U_2(4) \otimes U_3(4) \), i.e.,

\[ H = A_1 C_1 + A_2 C_2 + A_3 C_3 + A_{12} C_{12} + A_{123} C_{123} + B_{12} \hat{C}_{12} + B_{123} \hat{C}_{123} \]

\[ + \lambda_{12} M_{12} + \lambda_{13} M_{13} + \lambda_{23} M_{23}, \]

where \( A_1, A_2, A_3, A_{12}, A_{123}, B_{12}, B_{123}, \lambda_{12}, \lambda_{13}, \lambda_{23} \) are the expansion coefficients, which can be determined from the spectroscopic data.

We can obtain the classical Hamiltonian \( H_{cl} \) as the expectation value of \( H \) in the coherent state. The potential energy surface is defined as [14]

\[ V(q_1, q_2, q_3, p_1 = 0, p_2 = 0, p_3 = 0) \]

where \( q_i, p_i (i = 1, 2, 3) \) are the canonical coordinates and momenta, respectively.

Here, we use the following transformation [15–16]:

\[ q_i^2 = e^{-\beta_i (r_i - r_{i0})} (i = 1, 2, 3), \]

\[ a_1 \cdot a_3 = \frac{1}{\cosh \alpha_1 (\theta_1 - \theta_{10})}, \quad a_2 \cdot a_3 = \frac{1}{\cosh \alpha_2 (\theta_2 - \theta_{20})}, \]

where \( r_i \) is the \( i \)th bond coordinate, \( r_{i0} \) is the equilibrium bond length, \( \beta_i \) is the Morse parameter, \( \theta_i \) is the bond angle, and \( \theta_{i0} \) is the equilibrium bond angle. \( a_i \) is the unit vector
along the vector $q_i$; the value of $a_1 \cdot a_2$ is determined by the relations of $a_1$, $a_2$, and $a_3$. $\alpha_i$ is the parameter calculated according to the formula

$$
\alpha_i = \frac{2\cos h}{\sqrt{-(2(A_12 + A_{123})N_1 N_2 + 2(A_{13} + A_{123})N_1 N_3 - \frac{2}{5} A_{12} N_1 N_3 - \frac{2}{5} A_{13} N_1 N_3) N_1^2 + \frac{2}{5} A_{12} N_1 N_3 + u_i (\frac{1}{16} + \frac{1}{3} e + \frac{1}{5} e^2 + \frac{1}{5} e^3)}},
$$

where $N_i(i = 1, 2, 3)$ are the vibron numbers associated with the bond $i$. Here we defined $u_i = 1/m_i(i = 1, 2, 3)$. $m_1$, $m_2$ are the masses of the atoms at the end of the bond angle. $m_3$ is the mass of the atom at the apex. $v_i(i = 1, 2)$ is the frequency of molecular bending vibration.

$$
V(r_1, r_2, r_3, \theta_1, \theta_2) = (A_1 + A_{12} + A_{13} + A_{123})N_1^3 \left(2 - e^{-\beta_1 (r_1 - r_{1e})}\right) e^{-\beta_1 (r_1 - r_{1e})} + (A_2 + A_{12} + A_{13} + A_{123})N_2^3 \left(2 - e^{-\beta_2 (r_2 - r_{2e})}\right) e^{-\beta_2 (r_2 - r_{2e})} + (A_3 + 2A_{13} + A_{123})N_3^3 \left(2 - e^{-\beta_3 (r_3 - r_{3e})}\right) e^{-\beta_3 (r_3 - r_{3e})} + \frac{2}{5} A_{12} N_1 N_2 \left(2 - e^{-\beta_1 (r_1 - r_{1e})}\right) e^{-\beta_1 (r_1 - r_{1e})} \left[\left(\frac{1}{12} \frac{1}{3} \frac{1}{5} e + \frac{1}{5} e^2 + \frac{1}{5} e^3\right) + \frac{1}{12} \frac{1}{3} \frac{1}{5} e + \frac{1}{5} e^2 + \frac{1}{5} e^3\right]
$$

$$
= \frac{2}{5} A_{12} N_1 N_3 \left(2 - e^{-\beta_1 (r_1 - r_{1e})}\right) e^{-\beta_1 (r_1 - r_{1e})} \left[\left(\frac{1}{12} \frac{1}{3} \frac{1}{5} e + \frac{1}{5} e^2 + \frac{1}{5} e^3\right) + \frac{1}{12} \frac{1}{3} \frac{1}{5} e + \frac{1}{5} e^2 + \frac{1}{5} e^3\right]
$$

It is obvious that at $r_1 \to r_{1e}$, $r_2 \to r_{2e}$, $r_3 \to r_{3e}$ the potential energy surface has its global minimum, and the well depth at the minimum of the potential is

$$
D_e = -(2(A_1 + A_{12} + A_{13} + A_{123})N_1^3 + (A_3 + 2A_{13} + A_{123})N_3^3 - 2(A_{12} + A_{123})N_1^2 - 4(A_{13} + A_{123})N_1 N_3 + 2\lambda_{12} N_1 N_2 + 2\lambda_{13} N_1 N_3).
$$

The other stationary points of $V(r_1, r_2, r_3, \theta_1, \theta_2)$ are at, $r_1 = r_{1e}$, $r_2 \to r_{2\infty}$, $r_3 \to r_{3\infty}$, or at $r_1 \to r_{1e}$, $r_2 = r_{2e}$, $r_3 \to r_{3\infty}$, and $r_1 \to r_{1e}$, $r_2 \to r_{2\infty}$, $r_3 = r_{3e}$, which are the three valleys where two bonds are fully extended and another bond is at its equilibrium position. The depth of the $i$th valley is

$$
D_{e1} = -(A_1 N_1^2 + A_{12} N_1^2 + A_{13} N_1^2 + 0.5 \lambda_{12} N_1 N_2 + 0.5 \lambda_{13} N_1 N_3),
$$

$$
D_{e2} = -(A_2 N_2^2 + A_{12} N_2^2 + A_{13} N_2^2 + 0.5 \lambda_{12} N_1 N_2 + 0.5 \lambda_{13} N_1 N_3),
$$
AN ALGEBRAIC APPROACH FOR DETERMINING...

\begin{equation}
D_{e3} = -(A_3 N_2^2 + A_{123} N_3^2 + 0.5 \lambda_{13} N_1 N_3 + 0.5 \lambda_{23} N_1 N_3)
\end{equation}

Of course, for the dissociation plateau, the three bonds are broken when \( r_1 \rightarrow r_{1\infty}, r_2 \rightarrow r_{2\infty}, r_3 \rightarrow r_{3\infty} \).

We obtain the potential energy surface by using the semiclassical limit of the algebraic Hamiltonian. So by using Eq. (7) some properties of the potential surface can be discussed, and we can get the arbitrary order force constants. For simplicity, here we only calculate the second order force constants:

\begin{equation}
k_{r_1 r_1} = \frac{\partial^2 V}{\partial r_1^2} |_{r_1=r_1, r_2=r_2, r_3=r_3, \theta_1=\theta_{10}, \theta_2=\theta_{20}} = -2A_1 \beta_1^2 N_1^2 + A_{12}(-2 \beta_1^2 N_2^2 - 2 \beta_1^2 N_1 N_2) \\
+0.5 \lambda_{12} \beta_1^2 N_1 N_2 + 0.5 \lambda_{13} \beta_1^2 N_1 N_3 + A_{123}(-2 \beta_1^2 N_2^2 - 2 \beta_1^2 N_1 N_2 - 2 \beta_1^2 N_1 N_3),
\end{equation}

\begin{equation}
k_{r_2 r_2} = \frac{\partial^2 V}{\partial r_2^2} |_{r_1=r_1, r_2=r_2, r_3=r_3, \theta_1=\theta_{10}, \theta_2=\theta_{20}} = -2A_2 \beta_2^2 N_2^2 + A_{12}(-2 \beta_2^2 N_2^2 - 2 \beta_2^2 N_1 N_2) \\
+0.5 \lambda_{12} \beta_2^2 N_1 N_2 + 0.5 \lambda_{23} \beta_2^2 N_2 N_3 + A_{123}(-2 \beta_2^2 N_2^2 - 2 \beta_2^2 N_1 N_2 - 2 \beta_2^2 N_2 N_3),
\end{equation}

\begin{equation}
k_{r_3 r_3} = \frac{\partial^2 V}{\partial r_3^2} |_{r_1=r_1, r_2=r_2, r_3=r_3, \theta_1=\theta_{10}, \theta_2=\theta_{20}} = -2A_3 \beta_3^2 N_3^2 + 0.5 \lambda_{13} \beta_3^2 N_1 N_3 \\
+0.5 \lambda_{23} \beta_3^2 N_2 N_3 + A_{123}(-2 \beta_3^2 N_3^2 - 2 \beta_3^2 N_1 N_3 - 2 \beta_3^2 N_2 N_3),
\end{equation}

\begin{equation}
k_{\theta_1 \theta_1} = \frac{\partial^2 V}{\partial \theta_1^2} |_{r_1=r_1, r_2=r_2, r_3=r_3, \theta_1=\theta_{10}, \theta_2=\theta_{20}} = (-2A_{12} N_1 N_2 + A_{123}(-2 N_1 N_2 - 2 N_1 N_3) \\
+1.5 \lambda_{12} N_1 N_2 + 1.5 \lambda_{13} N_1 N_3) \alpha_1^2,
\end{equation}

\begin{equation}
k_{\theta_2 \theta_2} = \frac{\partial^2 V}{\partial \theta_2^2} |_{r_1=r_1, r_2=r_2, r_3=r_3, \theta_1=\theta_{10}, \theta_2=\theta_{20}} = (-2A_{12} N_1 N_2 + A_{123}(-2 N_1 N_2 - 2 N_1 N_3) \\
+1.5 \lambda_{12} N_1 N_2 + 1.5 \lambda_{23} N_2 N_3) \alpha_2^2.
\end{equation}

3. Application to the HCNO molecule

We now use this model to study the potential energy surface of the HCNO (Fig 1) molecule. The expansion coefficients \( A_1, A_2, A_3, A_{12}, A_{123}, B_{12}, B_{123}, \lambda_{12}, \lambda_{13}, \lambda_{23} \) in the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{The bond coordinates of fulminic acid (HCNO).}
\end{figure}
FIG. 2: The vibrational spectra of the molecule HCNO.

FIG. 3: The potential energy surface of HCNO with $r_1$ and $r_2$ ($r_3 = r_{3e}$, bond angles are at equilibrium).

Hamiltonian are obtained from fitting the spectra data using the first order approximation. The RMS (root-mean-square) of their values are listed in Table 1. In Table 2 the calculated levels of HCNO are listed and compared with the observed data [3]. Also in Fig. 2 we plotted the energy level of the quasi-linear tetratomic molecule HCNO. Hence, the Hamiltonian (2) is valid for describing the quasi-linear tetratomic molecule HCNO. The three-dimensional figure of the potential energy surface for the quasi-linear tetratomic molecule HCNO, with bond angles and one bond frozen at their equilibrium position, has the contours plotted, as
FIG. 4: The potential energy surface of HCNO with $r_1$ and $r_3$ ($r_2 = r_{2e}$, bond angles are at equilibrium).

FIG. 5: The contours corresponding to Fig. 3.

shown in Fig. 3, Fig. 4, Fig. 5, and Fig. 6.

In Table 3 we have given the calculated the values of $D_e$, $D_{ex}$, the force constants predicted by Eqs. (7)–(14), and those from other calculations [17].

From the simplest Hamiltonian, we obtained fairly realistic results, as shown in the above figures and tables. The potential energy surface includes some information of the bending motion, while some “chemical questions”, for example, the saddle point, can now be discussed. Work on these is in progress.
FIG. 6: The contours corresponding to Fig 4.

TABLE I: The fitting parameters of HCNO.
All parameters are in cm$^{-1}$, except $N_1$, $N_2$, $N_3$ which are dimensionless.

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Acknowledgements

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References

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TABLE II: Comparison of observed and calculated levels of HCNO.

\[ v’l \text{ means } v’, \Delta = \text{fit-obs.}, \delta = \left( \frac{\text{fit-obs.}}{\text{obs.}} \right) \times 100. \]

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TABLE III: The force constants of HCNO (\( aJ; \text{\AA}; \text{Rad} \)) and dissociation energy (eV).

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