

Force field calculations of acetonitrile using CNDO/force method

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Abstract. The redundancy-free internal valence force field (RFIVFF) of acetonitrile is reported using CNDO/force method. The initial force field is set up by taking the interaction and bending force constants from CNDO force field and transferring stretching force constants from the force fields of chemically related molecules. The final force field is obtained by refining the initial force field using vibrational harmonic frequencies of CH_3CN , $^{13}\text{CH}_3\text{CN}$, $\text{CH}_3^{13}\text{CN}$, $\text{CH}_3\text{C}^{15}\text{N}$, CD_3CN and $\text{CD}_3^{13}\text{CN}$. The final force field thus obtained is found to be excellent on the basis of frequency fit and potential energy distribution.

Keywords. Force field; normal coordinate analysis; acetonitrile; CNDO/force method.

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1. Introduction

Vibrational spectroscopic studies of acetonitrile have been a subject matter of keen investigations. Duncan *et al* (1978) reported gas phase infrared spectra of acetonitrile and its five isotopic species. Nakagawa and Shimanouchi (1962) reported vibration-rotation spectra of acetonitrile vapour in the region $200\text{--}6000\text{ cm}^{-1}$. Matrix isolated IR and Raman studies in solid Argon matrices at 20 K have been reported by Freedman and Nixon (1972) and Givan and Loewenschuss (1983). Infrared and Raman spectral studies of two crystal forms of CH_3CN and CD_3CN have been made at different temperatures by Pace and Noe (1968) and Marzocchi and Dobos (1974). Urey-Bradley force field was reported by Nakagawa and Shimanouchi (1962) while valence force field was evaluated by Fletcher and Shoup (1962). General valence force field using kinematic models have been reported by Aray and Murgich (1983). Molecular orbital (MO) studies on force fields of acetonitrile have been made by Dewar and Ford (1977), Pople *et al* (1981), Figeys *et al* (1979) and Blom (1978).

In the conventional method of normal coordinate analysis the initial force field is obtained by transferring the force constants from chemically related molecules. This force field is further refined to fit the vibrational frequencies. While it is quite justified to transfer the diagonal force constants from chemically related molecules, the transfer of off-diagonal elements is not reasonable because these force constants depend greatly on the nature of the molecule. Moreover, it is found that the final field depends largely on the set of initial force field. So, it is essential to have a reasonable initial force field. Our previous studies (Kanakavel *et al* 1976; Annamalai and Surjit Singh 1982a, b, c,

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1983a, b; Annamalai *et al* 1978, 1984; Jothi *et al* 1982; Brakaspathy *et al* 1985; Brakaspathy and Surjit Singh 1985, 1986a, b) using CNDO/force method predict the bending force constant, stretch-bend and bend-bend interaction constants correctly both in sign and magnitude. The stretch-stretch interaction constants are about 50% higher in magnitude and the stretching constants are exaggerated to 2–3.5 times. Ab-initio studies (Meyer and Pulay 1974) yield good results but require a lot of computation time. It was pointed out by IUPAC (1977) that the force constants corresponding to the coordinates expressed by redundancy conditions are indeterminate and recommendations were made that the redundancy-free coordinates should be used to have meaningful force fields. In our procedure the initial force field is set up by taking the bending and bend-bend interaction force constants from CNDO force field, scaling down the stretch-stretch interaction constants by a factor of 0.65 and transferring the stretching force constants from the force fields of chemically related molecules. The redundancy-free internal valence force field (RFIVFF) is then calculated by refining the initial force field using vibrational frequency data of various isotopic species.

In the data reported earlier force fields were calculated either by conventional normal coordinate analysis or by MO method. Figeys *et al* (1979) reported ab-initio force constants of acetonitrile in terms of internal coordinates involving HCH and HCC angles without considering redundancy aspects. Blom (1978) calculated ab-initio force constants using scale factors without iterating over the vibrational frequencies. In this paper, we report the redundancy-free internal valence force field of acetonitrile by considering five linear combinations of the six valence angles of the methyl group.

2. Computational details

The CNDO/force calculations were carried out using a modified form (Kanakavel *et al* 1976) of Pople's computer program CNINDO (Pople and Beveridge 1970). The molecular geometry was optimized using the steepest-descent method (Pulay and Torok 1973). The forces were then calculated by distorting the molecule, from the optimized reference geometry, in the positive and negative directions of the redundancy-free internal coordinates. The distortions considered were 0.01 Å, 1° and 2° for stretching, bending and torsional coordinates respectively. The CNDO force constants were then derived from the forces using the relationships given earlier (Kanakavel *et al* 1976). All calculations were performed on IBM 370/155 computer.

3. Results and discussion

The internal coordinates are illustrated in figure 1 and the redundancy-free internal coordinates are given in table 1. The initial force field was constructed according to the procedure given above. The harmonic frequencies reported by Duncan *et al* (1978) for acetonitrile and its 5 isotopic species CH_3CN , $^{13}\text{CH}_3\text{CN}$, $\text{CH}_3^{13}\text{CN}$, $\text{CH}_3\text{C}^{15}\text{N}$, CD_3CN and $\text{CD}_3^{13}\text{CN}$ were used to refine the force field. Since the number of force constants to be evaluated were less than the number of vibrational frequencies, iterations were carried out on all the force constants. A total of 27 force constants were

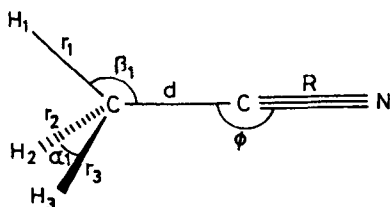


Figure 1. Internal coordinates of acetonitrile.

Table 1. Redundancy-free internal coordinates of acetonitrile.

Coordinate	Description
$v_{\text{CH}} = r_1$	CH stretch
$v_{\text{CH}} = r_2$	CH stretch
$v_{\text{CH}} = r_3$	CH stretch
$v_{\text{CC}} = d$	CC stretch
$v_{\text{CN}} = R$	CN stretch
$\delta_s \text{CH}_3 = * [3(1 + b^2)]^{-1/2} \times [b(\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)]$	CH_3 umbrella deform
$\delta'_s \text{CH}_3 = 6^{-1/2} (2\alpha_1 - \alpha_2 - \alpha_3)$	CH_3 sym. deform
$\gamma_{\parallel} \text{CH}_3 = 6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$	CH_3 rock
$\delta_a \text{CH}_3 = 2^{-1/2} (\alpha_2 - \alpha_3)$	CH_3 asym. deform
$\gamma_{\perp} \text{CH}_3 = 2^{-1/2} (\beta_2 - \beta_3)$	CH_3 rock
$\phi_{\text{CCN}} = \phi_x$	CCN linear bend
$\phi_{\text{CCN}} = \phi_y$	CCN linear bend

* $b = 3 \sin \beta \cos \beta / \sin \alpha$. The corresponding redundant coordinate is $[3(1 + b^2)]^{-1/2} [b(\alpha_1 + \alpha_2 + \alpha_3) + (\beta_1 + \beta_2 + \beta_3)]$.

refined using 72 vibrational frequencies. The computer program FPERT developed by Schachtschneider (1964) was used to refine the force constant after including the damped least-squares subroutine.

Two types of force fields FF1 and FF2 were evaluated. In the case of FF1, the signs of interaction constants are kept unaltered during the iterations and in FF2, the signs are allowed to vary for a better frequency fit. The redundancy-free internal valence force field is given in table 2. The force fields FF1 and FF2 are found to be very similar with respect to their sign and magnitude. Therefore, further discussion is henceforth confined to FF1 force field only.

The force constants for C-C and C≡N stretching vibrations are found to be 5.31 and 19.03 mdy \AA^{-1} respectively. This is in agreement with the valence force field values reported by Duncan *et al* (1978) (5.33 and 18.40 mdy \AA^{-1} for C-C and C≡N stretching respectively) and the ab-initio values reported by Blom (1978) (5.78 and 21.14 mdy \AA^{-1} for C-C and C≡N stretching respectively). The bending force constants are also predicted well in our calculations. The CH_3 umbrella deformation, CH_3 symmetry deformation, CH_3 rock and CCN-linear bending modes are found to have the values of 0.61, 0.61, 0.66 and 0.37 mdy $\text{\AA} \text{ rad}^{-2}$ respectively, which agree with

Table 2. Redundancy-free internal valence force field of acetonitrile.*

Description	CNDO/F	FF1	FF2	Expt. Duncan <i>et al</i> (1978)	ab-initio Blom (1978)	MUBFF Duncan (1964)
F1, 1	11.85	5.14	5.14	5.33	5.46	4.91
F1, 2	0.17	0.01	0.01	0.01	0.04	0.06
F1, 4	0.38	0.01	0.01	0.19	0.12	0.43
F1, 5	-0.05	-0.18	0.08	0.00	0.02	0.00
F1, 6	0.11	0.05	0.05	-0.03	0.06	-0.03
F1, 7	-0.22	-0.10	-0.10	-0.12	-0.15	-0.08
F1, 8	0.24	0.15	0.15	0.02	0.15	0.24
F1, 11	0.03	0.01	-0.01	-0.32	-0.01	0.0
F2, 3	0.17	0.01	0.01	-0.01	0.04	0.05
F2, 7	0.11	0.04	0.04	0.06	0.08	0.05
F2, 8	-0.12	-0.07	-0.07	-0.01	-0.07	-0.12
F2, 9	-0.19	-0.08	-0.08	-0.10	-0.13	-0.08
F2, 10	0.20	0.12	0.12	0.02	0.13	0.21
F2, 11	-0.12	-0.01	0.01	0.16	0.01	0.0
F2, 12	0.03	0.01	-0.01	-0.28	-0.01	0.0
F4, 4	17.15	5.31	5.31	5.33	5.78	5.07
F4, 5	1.67	0.63	0.63	0.24	-0.10	0.50
F4, 6	-0.39	-0.37	-0.37	-0.38	-0.48	-0.45
F5, 5	39.81	19.03	19.03	18.40	21.14	18.65
F5, 6	-0.06	-0.07	-0.07	-0.05	-0.03	0.0
F6, 6	0.71	0.61	0.61	0.61	0.75	0.50
F7, 7	0.74	0.61	0.61	0.54	0.66	0.53
F7, 8	-0.04	-0.02	0.02	0.03	-0.01	0.04
F7, 11	0.01	0.02	0.02	0.01	-0.01	0.0
F8, 8	0.62	0.66	0.66	0.69	0.84	0.75
F8, 11	0.14	0.10	0.10	-0.08	-0.12	0.0
F11, 11	0.73	0.37	0.37	0.37	0.45	0.31

F1, 1 = F2, 2 = F3, 3; F1, 2 = F1, 3; F1, 4 = F2, 4 = F3, 4; F1, 5 = F2, 5 = F3, 5; F1, 6 = F2, 6 = F3, 6; F2, 7 = F3, 7; F2, 8 = F3, 8; F2, 9 = F3, 9; F2, 10 = -F3, 10; F2, 11 = F3, 11; F2, 12 = -F3, 12; F7, 7 = F9, 9; F7, 8 = F9, 10; F7, 11 = F9, 12; F8, 8 = F10, 10; F8, 11 = F10, 12; F11, 11 = F12, 12.

* Units for force constants: Stretching and stretch-stretch in $\text{mdyn } \text{\AA}^{-1}$, stretch-bend in mdyn rad^{-1} , bending and bend-bend in $\text{mdyn } \text{\AA} \text{ rad}^{-2}$.

† The values given in columns 5, 6 and 7 are the redundancy-free internal force fields which are converted from their reported force fields.

the respective force constant values reported by Duncan *et al* (1978) (0.61, 0.54, 0.69 and 0.37 $\text{mdyn } \text{\AA} \text{ rad}^{-2}$). The corresponding ab-initio values (Blom 1978) are 0.75, 0.66, 0.84 and 0.45 $\text{mdyn } \text{\AA} \text{ rad}^{-2}$.

The interaction constants are also estimated correctly in the present calculations. For example, the value for C-C stretch/ CH_3 umbrella bend interaction constant is found to be $-0.37 \text{ mdyn rad}^{-1}$ which is very close to the valence force field (Duncan *et al* 1978) value of $-0.38 \text{ mdyn rad}^{-1}$. The ab-initio (Blom 1978) and Urey-Bradley (Duncan 1964) values for the same are reported as -0.48 and $-0.45 \text{ mdyn rad}^{-1}$

Table 3. Observed and calculated frequencies (cm^{-1}) and potential energy distributions (%) for acetonitrile*.

Observed	Calculated	$\Delta\nu$	PED
CH ₃ CN			
A			
3044.4	3044.5	-0.1	ν_{CH} (100)
2293.6	2293.9	-0.3	ν_{CN} (94)
1418.4	1418.0	0.4	$\delta'_2\text{CH}_3$ (104)
929.3	929.4	-0.1	ν_{CC} (87)
E			
3134.5	3135.6	-1.1	ν_{CH} (101)
1477.6	1476.7	0.9	$\delta'_2\text{CH}_3$ (96)
1062.0	1061.2	0.8	$\gamma_{\parallel}\text{CH}_3$ (84)
365.0	365.6	-0.6	ϕ_{CCN} (100), $\gamma_{\parallel}\text{CH}_3$ (15%)

* Similar data for its 5 isotopic species with ^2H , ^{13}C and ^{15}N substitution have also been calculated and can be made available on request.

respectively. The CH₃ rock/CCN linear bend interaction constant is found to be $0.10 \text{ m dyn } \text{\AA} \text{ rad}^{-1}$ whereas the experimental (Duncan *et al* 1978) and ab-initio (Blom) methods predict these values as -0.08 and $-0.12 \text{ m dyn } \text{\AA} \text{ rad}^{-2}$. In UBFF this value is constrained to zero. Furthermore, while the present investigation envisages a strong interaction for $\nu_{\text{CC}}/\nu_{\text{CN}}$ mode ($0.63 \text{ m dyn } \text{\AA}^{-1}$), ab-initio calculation (Blom 1978) predicts a negative value ($-0.1 \text{ m dyn } \text{\AA}^{-1}$) for this interaction.

The calculated and observed frequencies alongwith potential energy distributions are reported in table 3. It is observed that most of the bands are uncoupled having more than 80% contribution from single redundancy-free internal coordinates. However, the band at 365 cm^{-1} is found to have significant contribution from CCN linear bend (100%) and CH₃ rock (15%) coordinates. In deuterated species the CC stretching and CD₃ umbrella bending coordinates are found to have significant contributions for the band observed at 838.6 cm^{-1} . The agreement between calculated and observed frequencies is within $\pm 1 \text{ cm}^{-1}$.

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