

## Thermal molecular beam matrix spectroscopy of cyclobutanol: temperature dependence of lineshapes and the conformation problem

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**Abstract**—Thermal molecular beam spectra of cyclobutanol isolated in Ar and Xe matrices and the temperature dependence of the  $\nu(\text{OH})$  Raman line are reported. Six matrix bands are shown by lineshape analysis to consist of 4–6 components which systematically decrease and increase with increasing temperature of the molecular beam source. Data on lineshape parameters and relative intensities are reported. Likewise the  $\nu(\text{OH})$  Raman band is shown to consist of four components which behave with respect to temperature dependence analogously to the matrix bands. The results will be discussed in terms of two models.

### 1. INTRODUCTION

Cyclobutanol is a molecule featuring two finite degrees of freedom, the 4-ring puckering mode and the OH group internal rotation. Principally it might possess localized conformations which can be distinguished by various spectroscopic techniques. It raises the question how kinetic and potential coupling expresses itself in vibrational and rotational spectra. At first sight such couplings are expected to lead to remarkable effects.

So far cyclobutanol has been subject to relatively few investigations. Vibrational spectra of cyclobutanol and four of its deuterium modifications in the range  $4000\text{--}70\text{ cm}^{-1}$  have been reported by DURIG and GREEN [1] and by DURIG *et al.* [2]. Assignments of the spectra have been proposed by these authors based on isotope shifts and empirical group frequency rules. In particular, it was inferred from complicated band contours (splittings) of the  $\nu(\text{OH})$  and the  $\delta(\text{COH})$  bands that the molecule exists in at least three conformeric forms, differing in the conformation of both the OH group and the 4-ring.

In a microwave spectroscopy investigation of the parent species SHERIDAN *et al.* [3] identified one conformer, but the question of the existence of further localized conformations was left open. For the identified species the conformation “*trans* OH with equatorial C–O bond” was derived.

In this paper experiments will be reported which aim at identification of conformers either reported earlier or possibly new. It has been shown some time ago that rotational conformers may be frozen in rare gas matrices from thermal molecular beams in the thermal equilibrium of the conformers prevailing in the Knudsen cell [4, 5]. It has not yet been established whether unstable conformations of 4-membered carbon rings may be trapped from hot molecular beams. However, SQUILLACOTE *et al.* [6] have reported thermal molecular beam-matrix experiments, which were interpreted as trapping of both chair and twist-boat forms of cyclohexane.

Cyclobutanol appears to represent a favorable molecule for such experiments since besides axial and equatorial substituent conformation it offers a possibility for the study of the problem of trapping of unstable OH conformations. The latter problem appears to be a non-resolved question since such conformations seem to equilibrate in rare gas matrices even at LHe temperature, or to interconvert under i.r. irradiation [7–10]. It will be shown that thermal molecular beams yield matrix spectra of cyclobutanol, which feature pronounced and systematic temperature dependence of the complex line shapes of the matrix bands. Comparison with the temperature dependence of Raman gas spectra yields a close analogy of the complex lineshape behavior.

### 2. EXPERIMENTAL

#### 2.1. Chemicals

Cyclobutanol samples were prepared along published procedures from diazomethane and ketene and subsequent reduction by  $\text{LiAlH}_4$  or was purchased\*. Samples were purified by means of a spinning band column and found by GLC to contain no detectable impurities. Cyclobutanol  $\text{Od}_1$  was produced by 3–4 exchanges with slightly alkaline ( $\text{NaOH}$ )  $\text{D}_2\text{O}$ . In order to diminish exchange in spectroscopic measurements, cells and vacuum manifolds were conditioned by several  $\text{D}_2\text{O}$ -treatments. For matrix spectroscopy Ar and Xe (5.5 purity, Matheson) were used without further purification.

#### 2.2. Instrumentation

Matrix spectroscopy experiments were carried out by means of a homebuilt LHe bath cryostat built into a Perkin–Elmer model 325 spectrophotometer. Thermal molecular beams of cyclobutanol were generated by a Knudsen cell heated to temperatures between ambient and  $300^\circ\text{C}$ . At temperatures above  $320^\circ\text{C}$  decomposition of cyclobutanol to ethylene, acetaldehyde and vinyl alcohol is observed. The temperature of the molecular beam was measured by a miniature coax thermocouple (thermocox, Philips AG) placed in front of the Knudsen orifice. The rate of deposition was measured with the aid of a small HeNe laser [11]. Cyclobutanol vapor was admitted to the Knudsen cell from a

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thermostatted ampoule, yielding a vapor pressure of 3.7 Torr, and Ar was admitted through four concentric nozzles from a gas reservoir kept at 180 Torr. Gas-phase Raman spectra were taken with a homebuilt Raman spectrometer consisting of a SPEX Model 14001 double monochromator, CRL model 52 and 12 Ar ion lasers, photon counting electronics and a heatable focusing gas cell (suprasil). For measurement the cyclobutanol samples were fused off in the cell and the temperature of the cell oven was controlled ( $\pm 1^\circ\text{C}$ ) by various thermostating systems. Measurements were made by a homebuilt digitalizer system recording data on punched paper tape, which was then processed on a Wang 2200 computer system through digital filtering and pooling of a 4–9 spectra.

### 2.3. Lineshape analysis

In the present work intense use has been made of lineshape analysis of vibrational transitions of cyclobutanol isolated in rare gas matrices and gas phase. Since these spectra were taken with spectral slit width of  $\approx 0.5\text{ cm}^{-1}$  (FWHM) and true linewidth of matrix bands in the average amount to less

than  $0.2\text{ cm}^{-1}$  (FWHM), observed lineshapes are dominated by the spectral slit. In order to derive information about composition of complex matrix band shapes from up to five component bands, a program package comprising digitization of graphically recorded bands, calculation of optical density (transmission) after correction for base line, approximation of observed optical density by a linear combination of Lorentz or Gaussian or mixed Lorentz–Gaussian (sum or product) or modified Lorentz band profiles by least squares, smoothing of original data, peak finding, etc. has been developed [12].

### 3. RESULTS

In Fig. 1 the Ar matrix spectra observed with two different molecular beam source temperatures and the Xe matrix spectrum are reproduced. The Raman gas spectrum in the  $\nu(\text{OH})$  region taken at six temperatures is reproduced in Fig. 2.

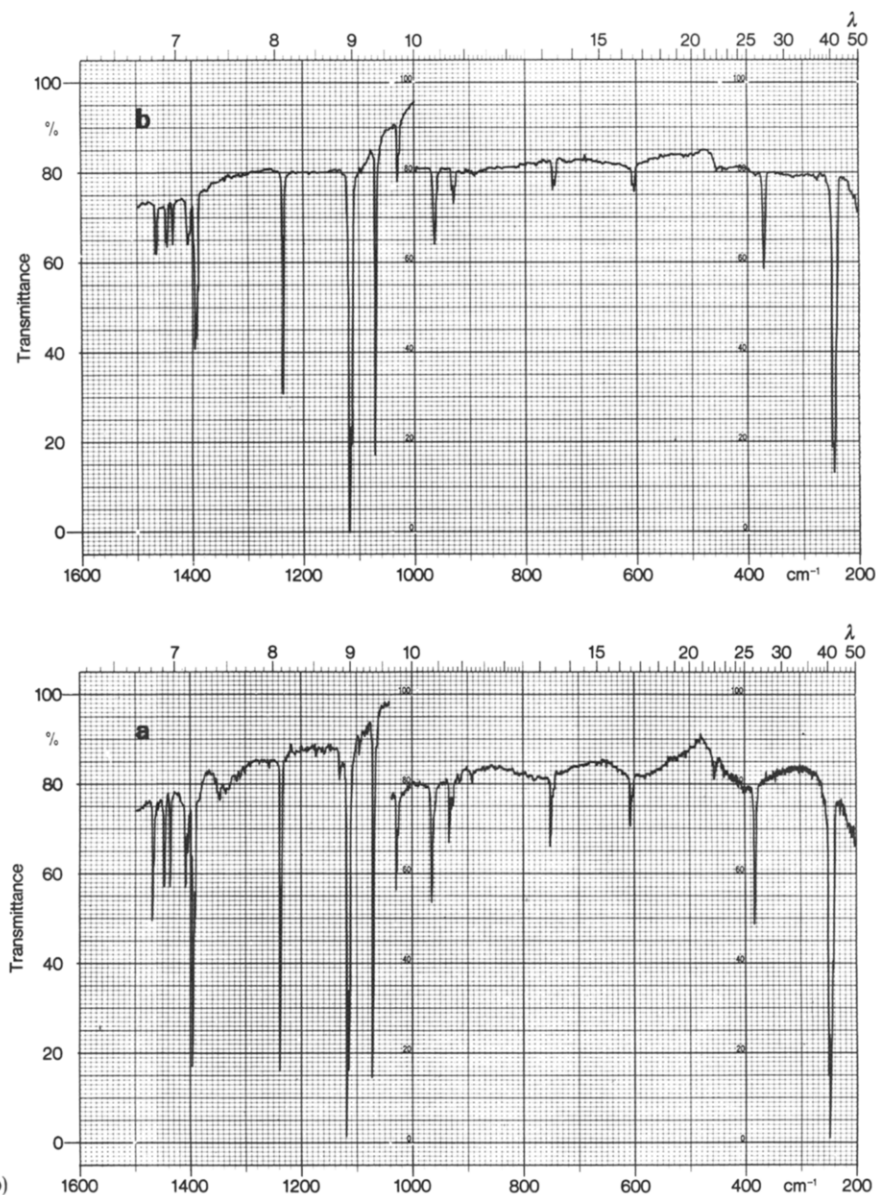


Fig. 1(a), (b)

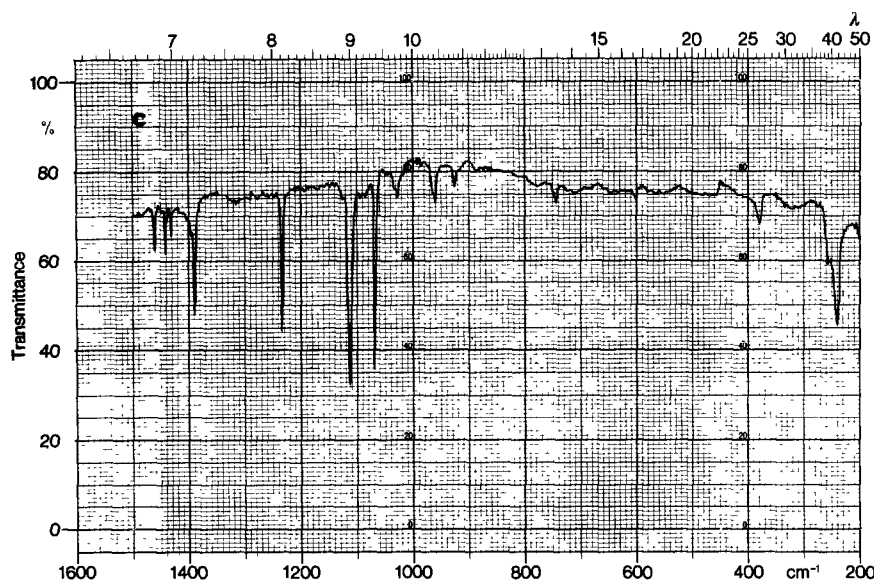


Fig. 1. Cyclobutanol: Ar(s) and cyclobutanol: Xe(s) i.r. spectra, dependence on Knudsen cell temperature.  $d = 405 \mu\text{m}$ ,  $M/A \approx 1000$ , average spectral slit  $0.5 \text{ cm}^{-1}$  (HWHM) (a) Ar(s),  $T_{\text{KC}} = 20^\circ\text{C}$ ; (b) Ar(s),  $T_{\text{KC}} = 281^\circ\text{C}$ ; (c) Xe(s),  $T_{\text{KC}} = 20^\circ\text{C}$ ,  $d = 40 \mu\text{m}$ ,  $M/A \approx 250$ .

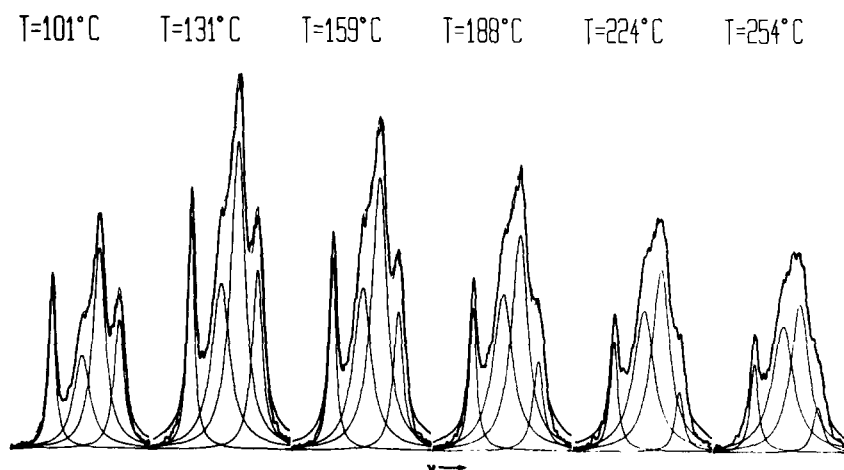


Fig. 2. Raman spectrum of cyclobutanol (g): temperature dependence of the OH stretching band. Spectral slit width  $\approx 1.5 \text{ cm}^{-1}$  (FWHM), each spectrum is derived from pooling of 4 measurements, spectral range  $3640\text{--}3680 \text{ cm}^{-1}$ , peak frequencies see Table 11.

#### 4. ANALYSIS OF RESULTS

##### 4.1. Lineshape of matrix bands

Closer inspection of the line profiles of the matrix absorption bands reveals a rich variety of structure of nearly all bands, which furthermore depends strongly on the molecular beam source temperature. Figure 3 documents this behavior.

As generally observed, line profile analysis of Ar matrix bands (an analogous behavior is found for Xe matrix bands) meets the problem of fixing the number

of relevant component bands. In this work the following rules have been adopted:

(i) as a lineshape function, usually the Cauchy-Lorentz function [ $\bar{\nu}_r$  and  $\gamma$  stand for resonance frequency and linewidth parameter (HWHM), respectively] is chosen,

$$g(\tilde{\nu}) = \frac{1}{\pi} \frac{\gamma}{(\tilde{\nu} - \bar{\nu}_r)^2 + \gamma^2}. \quad (1)$$

In most cases this lineshape function has systematically too large values in the wings ( $|\tilde{\nu} - \bar{\nu}_r| > 5\gamma$ ), therefore

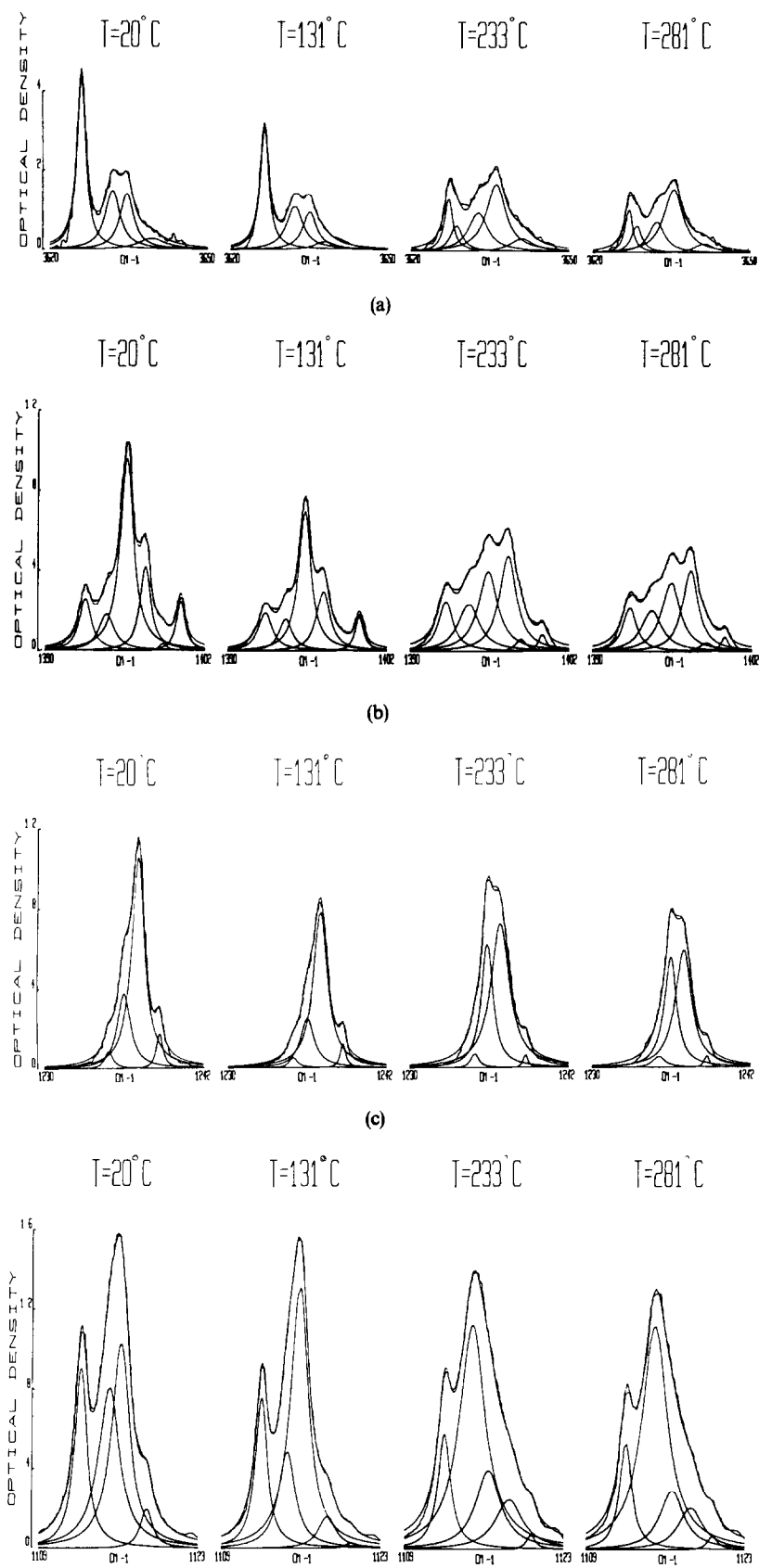


Fig. 3(a)–(d)

(d)

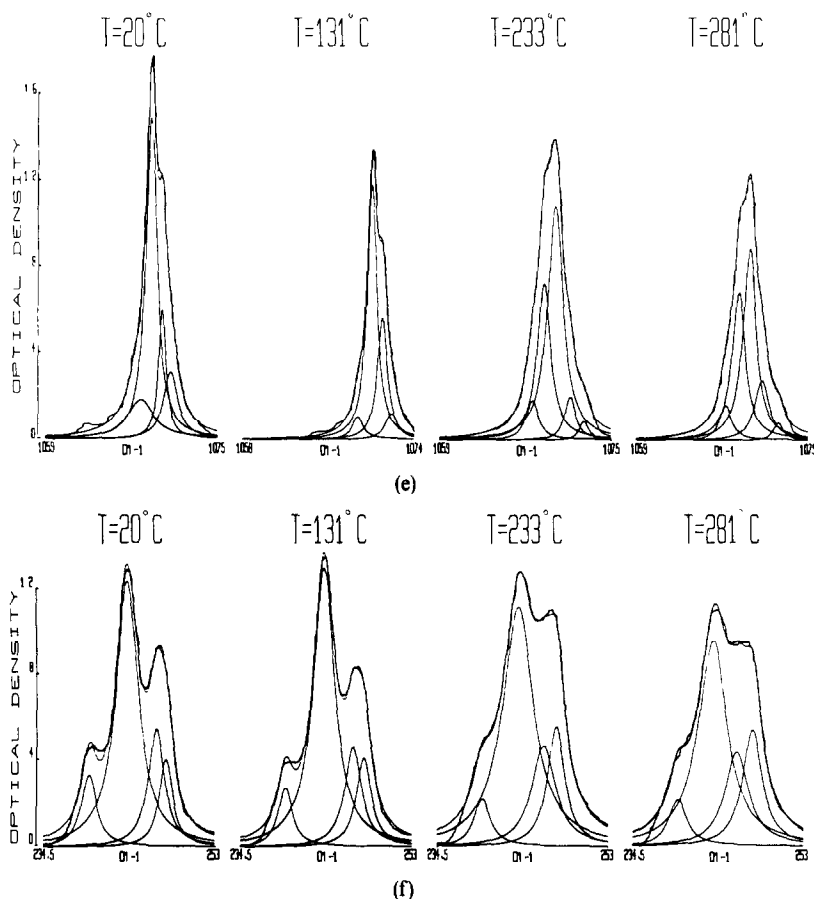


Fig. 3. Cyclobutanol: Ar(s) i.r. spectra: line profile analysis. For conditions see Fig. 1. (a)  $\nu(\text{OH})$ ; (b)  $\delta(\text{CH})$ , in-plane; (c)  $\delta(\text{COH})$ ; (d)  $\nu(\text{CO})$ ; (e) ring deformation; (f) OH-torsion.

in some cases a modified Cauchy-Lorentz shape has been used:

$$g(\tilde{\nu}) = N\gamma[\gamma^2 + (\tilde{\nu} - \tilde{\nu}_r)^2 + \beta\gamma^{-2}(\tilde{\nu} - \tilde{\nu}_r)^4]^{-1} \quad (2)$$

with the normalization factor

$$N = \pi^{-1} [2(1-4\beta)]^{1/2} \{ -[1 - (1-4\beta)^{1/2}]^{1/2} + [1 + (1-4\beta)^{1/2}]^{1/2} \}^{-1};$$

(ii) as a rule the minimum number of bands was admitted which reproduces acceptably the observed band contour;

(iii) the observed (apparent) lineshape has not been deconvoluted by the spectral slit function. Instead the experimental band contours were directly decomposed into Lorentzian components. As a consequence the latter represent apparent, not true, Lorentzians. From numerical analysis it has been found that the band areas are much less affected by the spectral slit function, even if peak absorption and line width parameters are strongly influenced;

(iv) for all band contours a linear base line was adopted. The base line was required to equal the transmission  $1-3 \text{ cm}^{-1}$  above and below the  $T \approx 0.95$  points of the band contour. Furthermore the contour

was digitized at approximately  $0.1 \text{ cm}^{-1}$  intervals.

Figure 3 represents the results of the lineshape analysis process for six matrix bands of cyclobutanol: Ar, namely  $\nu(\text{OH}) - 3630 \text{ cm}^{-1}$ ,  $\delta(\text{CH}) - 1395 \text{ cm}^{-1}$ ,  $\delta(\text{COH}) - 1237 \text{ cm}^{-1}$ ,  $\nu(\text{C-O}) - 1115 \text{ cm}^{-1}$ , ring bend  $- 1070 \text{ cm}^{-1}$  and  $\tau(\text{C-OH}) - 243 \text{ cm}^{-1}$ . These should be commented upon as follows:

(i) all six band contours have been decomposed into four components, but in some cases one or two further weak bands seem to be required;

(ii) use of Gaussian or Lorentzian-Gaussian mixed line shape functions was found to yield higher r.m.s. deviation in the central part of the band complexes but did not significantly reduce the systematic wing deviations;

(iii) approximation of experimental contours in all cases appears satisfactory in the central part, in the wings the simulated contours appear to produce systematically higher optical density than measured experimentally. Similar behavior has been observed by lineshape measurements with very high resolution [13-15]. This finding initiated the use of the modified lineshape function (2), which has been suggested on various occasions in the literature [16, 17].

Numerical values of the lineshape parameters of six transitions of cyclobutanol: Ar(s) are collected in

Tables 1–6 and should be complemented by the following comments:

(i) the information given on intensity was obtained by division of the (apparent) integrated optical density of each component by the total integrated optical density, the latter taken as the sum of the integrated optical densities of all components;

(ii) from the numerical data one recognizes fairly clearly that the lineshape parameter  $\gamma$  of most components increases with increasing Knudsen cell temperature;

(iii) the band contours obtained with the highest

molecular beam temperature require rather systematically five components for an acceptable fit;

(iv) the components of all six analyzed bands clearly fall into subsets with either increasing or decreasing relative intensity. This behavior is documented by Fig. 4.

Results from lineshape analysis of four vibrational bands of cyclobutanol: Xe(s) as a function of Knudsen cell temperature are collected in Tables 7–10. Inspection of the data yields:

(i) the Xe matrix bands consist of the same number of discernible components as do the Ar matrix bands;

Table 1. Cyclobutanol: Ar(s): lineshape parameters for  $\nu(\text{OH})$

$T(^{\circ}\text{C})$	$I(\text{exp})^{*+}$	$I(\text{LSA})^{*+}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	2.917	3.019	1	0.420	0.96	3626.6	0.479	1.49E-2
			2	0.241	1.61	3632.3	0.236	
			3	0.212	1.51	3634.9	0.211	
			4	0.082	2.95	3639.3	0.075	
131	1.949	2.036	1	0.296	0.95	3626.0	0.439	9.01E-3
			2	0.197	1.81	3631.6	0.284	
			3	0.148	1.56	3634.4	0.216	
			4	0.045	2.24	3637.1	0.061	
233	2.440	2.486	1	0.122	0.93	3626.8	0.147	6.90E-3
			2	0.203	2.12	3632.2	0.245	
			3	0.359	2.12	3635.5	0.418	
			4	0.082	2.54	3640.2	0.090	
			5	0.084	1.33	3628.3	0.100	
281	1.985	2.053	1	0.934	0.87	3626.6	0.137	5.77E-3
			2	0.139	1.81	3631.9	0.197	
			3	0.347	2.17	3635.1	0.483	
			4	0.052	2.22	3640.8	0.071	
			5	0.079	1.19	3628.1	0.114	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

$^{\dagger}$ Unit  $\text{cm}^{-1}$ .

Table 2. Cyclobutanol: Ar(s): lineshape parameters for ring bend at  $1070\text{ cm}^{-1}$

$T(^{\circ}\text{C})$	$I(\text{exp})^{*+}$	$I(\text{LSA})^{*+}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	5.676	5.673	1	0.257	1.40	1068.0	0.152	3.08E-2
			2	0.876	0.59	1069.0	0.554	
			3	0.235	0.39	1069.9	0.147	
			4	0.230	0.73	1070.7	0.147	
131	3.830	3.811	1	0.060	0.56	1067.8	0.055	2.32E-2
			2	0.596	0.50	1069.1	0.598	
			3	0.289	0.51	1070.0	0.278	
			4	0.078	0.66	1070.8	0.069	
233	5.359	5.437	1	0.117	0.64	1068.0	0.078	1.89E-3
			2	0.506	0.70	1068.9	0.315	
			3	0.871	0.80	1069.9	0.520	
			4	0.111	0.55	1071.2	0.065	
			5	0.040	0.46	1072.4	0.022	
281	4.454	4.510	1	0.097	0.60	1067.6	0.074	1.67E-2
			2	0.468	0.69	1068.7	0.332	
			3	0.591	0.66	1069.7	0.428	
			4	0.202	0.73	1070.8	0.138	
			5	0.040	0.50	1072.2	0.028	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

$^{\dagger}$ Unit  $\text{cm}^{-1}$ .

Table 3. Cyclobutanol: Ar(s): lineshape parameters for  $\nu(\text{CO})$ 

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	7.487	7.492	1	0.592	0.65	1112.5	0.229	2.07E-2
			2	0.902	1.11	1115.0	0.340	
			3	0.996	0.96	1116.0	0.381	
			4	0.127	0.63	1118.3	0.050	
131	6.886	6.895	1	0.480	0.63	1112.3	0.214	1.54E-2
			2	0.432	0.88	1114.6	0.186	
			3	1.252	0.95	1115.6	0.530	
			4	0.148	0.90	1118.1	0.062	
			5	0.019	0.64	1120.2	0.008	
233	8.965	9.027	1	0.394	0.68	1112.5	0.160	1.99E-2
			2	1.547	1.37	1114.9	0.533	
			3	0.524	1.31	1116.3	0.182	
			4	0.357	1.42	1118.1	0.115	
			5	0.034	0.46	1120.0	0.011	
281	7.243	7.285	1	0.345	0.63	1112.4	0.141	1.79E-2
			2	1.531	1.35	1114.9	0.595	
			3	0.376	1.25	1116.4	0.146	
			4	0.273	1.29	1118.1	0.103	
			5	0.037	0.53	1120.0	0.015	

\*Total integral over band group, optical density of transmission spectrum corrected for base line.

†Unit  $\text{cm}^{-1}$ .Table 4. Cyclobutanol: Ar(s): lineshape parameters for  $\delta(\text{COH})$ 

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	3.218	3.282	1	0.032	0.37	1235.4	0.037	2.18E-2
			2	0.230	0.61	1236.6	0.226	
			3	0.642	0.61	1237.6	0.674	
			4	0.052	0.29	1239.3	0.062	
131	2.840	2.917	1	0.020	0.38	1235.4	0.023	1.68E-2
			2	0.162	0.65	1236.5	0.222	
			3	0.534	0.68	1237.5	0.714	
			4	0.031	0.25	1239.3	0.041	
233	3.150	3.280	1	0.025	0.35	1235.7	0.029	1.87E-2
			2	0.334	0.53	1236.6	0.361	
			3	0.615	0.85	1237.6	0.597	
			4	0.014	0.21	1239.5	0.013	
281	2.549	2.666	1	0.032	0.57	1235.6	0.038	1.42E-2
			2	0.324	0.59	1236.4	0.382	
			3	0.451	0.77	1237.4	0.562	
			4	0.014	0.23	1239.3	0.018	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

†Unit  $\text{cm}^{-1}$ .

(ii) the contours of the Xe matrix bands spread systematically over  $2\text{--}3\text{ cm}^{-1}$  wider frequency ranges than Ar matrix bands. This results from both larger line width and from larger splittings between components;

(iii) linewidth parameters of low frequency Xe matrix bands are larger by factors 2–4 than those of corresponding Ar bands, e.g. for the components of the torsional OH mode one finds linewidth parameters of  $3.0\text{--}4.6\text{ cm}^{-1}$  and  $0.85\text{--}1.5\text{ cm}^{-1}$  in Xe and Ar, respectively ( $T_{\text{KC}} = 20^{\circ}\text{C}$  spectrum).

#### 4.2. $\nu(\text{OH})$ -Raman band

Application of the lineshape analysis to the contours of the  $\nu(\text{OH})$ -Raman band observed at six temperatures yields the components drawn in Fig. 2 and the line shape parameters collected in Table 11. These data should be commented upon as follows:

(i) the  $\nu(\text{OH})$  band appears to consist of at least four components;

(ii) the four components fall into two pairs with respect to temperature dependence: one pair with

Table 5. Cyclobutanol: Ar(s): lineshape parameters for  $\delta(\text{CH})$ 

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	4.216	4.276	1	0.153	0.59	1392.2	0.118	2.52E-2
			2	0.138	0.76	1394.0	0.099	
			3	0.646	0.67	1395.7	0.527	
			4	0.226	0.54	1397.3	0.168	
			5	0.011	0.32	1398.7	0.008	
			6	0.107	0.43	1400.2	0.086	
131	3.215	3.272	1	0.136	0.72	1392.1	0.126	1.21E-2
			2	0.107	0.67	1393.9	0.103	
			3	0.449	0.64	1395.5	0.490	
			4	0.209	0.70	1397.1	0.206	
			5	0.004	0.40	1398.7	0.004	
			6	0.074	0.43	1400.2	0.071	
233	4.098	4.159	1	0.184	0.74	1391.9	0.136	1.26E-2
			2	0.253	1.08	1393.9	0.185	
			3	0.392	0.99	1395.5	0.297	
			4	0.414	0.87	1397.2	0.330	
			5	0.034	0.55	1398.3	0.029	
			6	0.034	0.40	1400.1	0.025	
281	3.298	3.370	1	0.155	0.72	1392.0	0.141	1.13E-2
			2	0.219	1.08	1393.9	0.196	
			3	0.336	0.98	1395.6	0.303	
			4	0.335	0.83	1397.3	0.307	
			5	0.030	0.68	1398.7	0.026	
			6	0.029	0.39	1400.3	0.025	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

 $\dagger$ Units  $\text{cm}^{-1}$ .Table 6. Cyclobutanol: Ar(s): lineshape parameters for  $\tau(\text{OH})$ 

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	9.520	9.658	1	0.331	0.99	239.2	0.104	2.17E-2
			2	1.799	1.44	243.3	0.599	
			3	0.346	0.85	247.5	0.122	
			4	0.565	1.03	246.5	0.176	
131	8.434	8.587	1	0.248	0.90	238.9	0.084	1.97E-2
			2	1.79	1.37	243.0	0.608	
			3	0.400	0.97	247.4	0.138	
			4	0.505	1.08	246.2	0.171	
233	10.447	10.583	1	0.232	1.07	239.3	0.062	2.39E-2
			2	2.222	1.98	243.1	0.578	
			3	0.614	1.10	247.3	0.162	
			4	0.716	1.52	245.9	0.198	
281	9.134	9.281	1	0.242	1.13	239.2	0.073	2.03E-2
			2	1.753	1.82	242.8	0.530	
			3	0.663	1.22	247.1	0.198	
			4	0.653	1.49	245.4	0.198	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

 $\dagger$ Unit  $\text{cm}^{-1}$ .Table 7. Cyclobutanol: Xe(s): lineshape parameters for  $\delta(\text{CH})$ 

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	1.651	1.719	1	0.076	1.13	1389.6	0.133	4.68E-3
			2	0.167	1.24	1390.9	0.293	
			3	0.219	1.74	1392.3	0.372	
			4	0.058	1.46	1398.5	0.108	
			5	0.006	1.04	1402.2	0.006	
			6	0.054	2.06	1406.1	0.088	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.

 $\dagger$ Unit  $\text{cm}^{-1}$ .



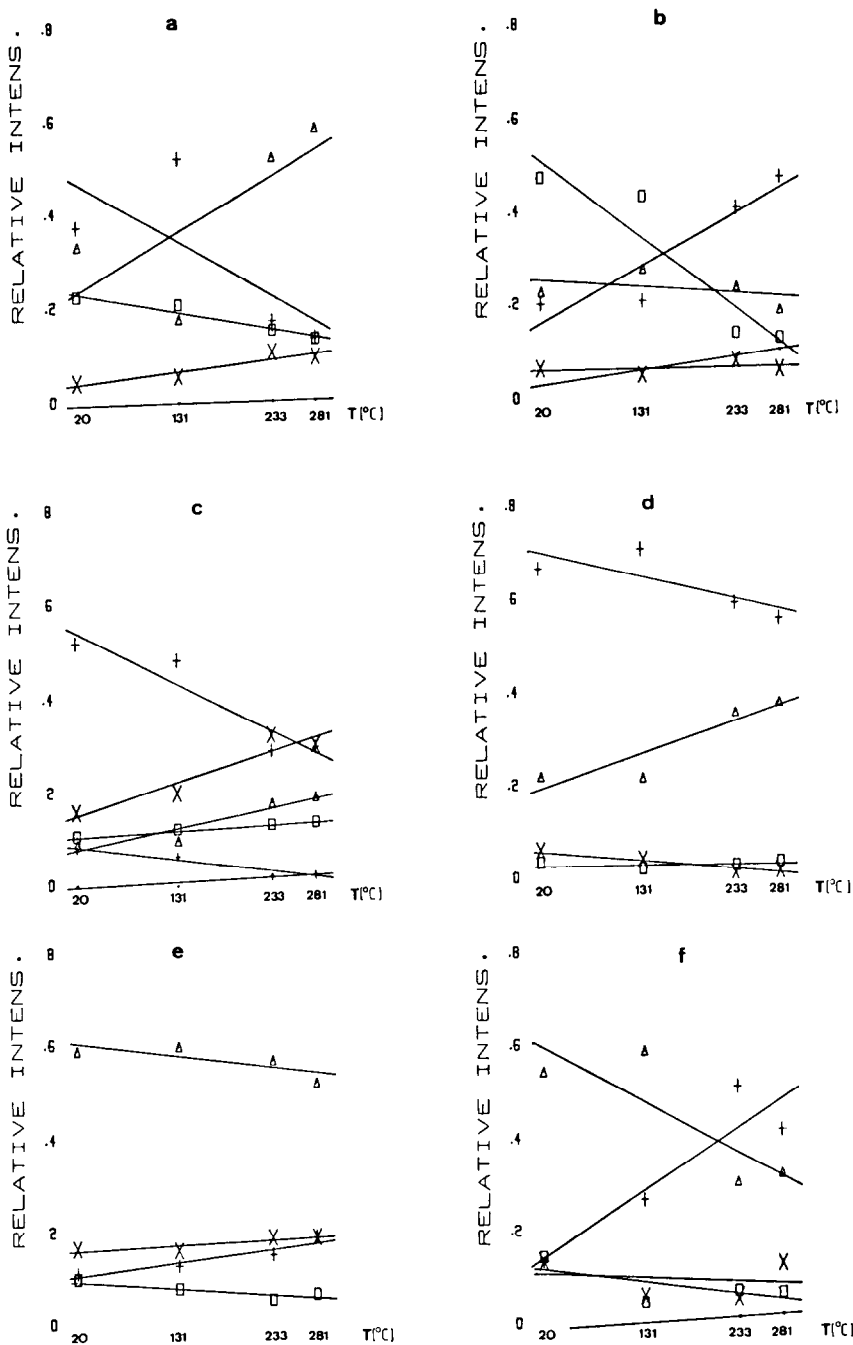


Fig. 4. Cyclobutanol: Ar(s): dependence of intensity components of complex vibrational bands on molecular beam source temperature. For experimental conditions see Fig. 1. (a)  $\nu(\text{CO})$ ; (b)  $\nu(\text{OH})$ ; (c)  $\delta(\text{CH})$ , in-plane; (d)  $\delta(\text{COH})$ ; (e) OH-torsion; (f) ring deformation.

Table 8. Cyclobutanol: Xe(s): lineshape parameters for  $\nu(\text{CO})$

$T(^{\circ}\text{C})$	$I(\text{exp})^{*†}$	$I(\text{LSA})^{*†}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\tilde{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	3.623	3.792	1	0.169	1.84	1109.9	0.162	1.16E-2
			2	0.594	1.88	1112.6	0.425	
			3	0.417	1.93	1114.9	0.300	
			4	0.148	1.26	1117.9	0.113	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.  
†Unit  $\text{cm}^{-1}$ .

Table 9. Cyclobutanol: Xe(s): lineshape parameters for  $\tau(\text{OH})$

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	5.925	5.991	1	0.346	3.48	239.9	0.156	8.77E-3
			2	0.625	3.02	243.2	0.293	
			3	0.679	4.63	247.3	0.305	
			4	0.556	4.58	259.0	0.245	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.  
†Unit  $\text{cm}^{-1}$ .

Table 10. Cyclobutanol: Xe(s): lineshape parameters for  $\delta(\text{COH})$

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\dagger}$	$I(\text{LSA})^{*\dagger}$	Band	$A^{\dagger}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s.
20	1.346	1.469	1	0.137	0.86	1233.8	0.311	8.59E-3
			2	0.264	1.02	1235.3	0.561	
			3	0.045	0.68	1236.8	0.102	
			4	0.012	0.43	1237.9	0.026	

\*Total integral over band group; optical density of transmission spectrum corrected for base line.  
†Unit  $\text{cm}^{-1}$ .

Table 11. Lineshape parameters for  $\nu(\text{OH})$  Raman band

$T(^{\circ}\text{C})$	$I(\text{exp})^{*\ddagger}$	$I(\text{LSA})^{*\ddagger}$	Band	$A^{\S}$	$\gamma^{\dagger}$	$\bar{\nu}_r^{\dagger}$	$I(\text{rel.})$	r.m.s. $^{\S}$
101	2519.5	2572.3	1	145.1	1.37	3642.3	0.170	3.79
			2	209.2	3.42	3652.7	0.233	
			3	351.1	2.66	3658.6	0.397	
			4	178.4	2.10	3665.6	0.200	
131	4213.3	4298.7	1	176.1	1.40	3641.9	0.149	5.83
			2	391.4	3.66	3652.3	0.273	
			3	567.9	3.16	3658.1	0.407	
			4	187.9	2.06	3664.9	0.171	
159	3721.4	3813.5	1	142.1	1.51	3641.7	0.138	5.51
			2	427.8	4.16	3652.2	0.292	
			3	484.7	3.41	3658.0	0.426	
			4	125.2	2.12	3664.7	0.143	
188	3287.1	3364.6	1	142.0	1.52	3641.7	0.126	4.79
			2	428.0	4.16	3652.2	0.356	
			3	483.9	3.41	3658.0	0.410	
			4	124.8	2.12	3664.7	0.108	
224	2841.2	2911.8	1	114.3	1.59	3642.0	0.119	4.13
			2	446.0	4.74	3652.6	0.378	
			3	367.8	3.29	3658.5	0.432	
			4	86.7	2.14	3665.1	0.071	
254	2494.7	2566.8	1	116.1	1.62	3642.0	0.112	3.87
			2	394.4	4.26	3652.5	0.407	
			3	447.3	3.76	3658.4	0.412	
			4	70.3	1.77	3665.1	0.069	

\*Total integ. over band group.  
†Unit  $\text{cm}^{-1}$ .  
‡Unit number of counts  $\text{cm}^{-1}/3 \text{ s}$ .  
§Unit number of counts/3 s.

increasing and one pair with decreasing (relative integrated) intensity *vs.* temperature. This is shown further in Fig. 5. Comparison with Fig. 4 reveals a close similarity to the *T*-dependence of the components of matrix band contours.

5. DISCUSSION

At the present time the data presented above appear to admit two interpretations:

- (i) existence of several conformations which can be trapped in rare gas matrices from thermal molecular beams;
  - (ii) existence of several sites of cyclobutanol in Ar and Xe matrices, which can be occupied in dependence of the translational and/or possibly vibrational energy of the molecular beam.
- Both models appear to fulfil and to contradict, respectively, some empirical rules.
- If several conformations of cyclobutanol were pre-

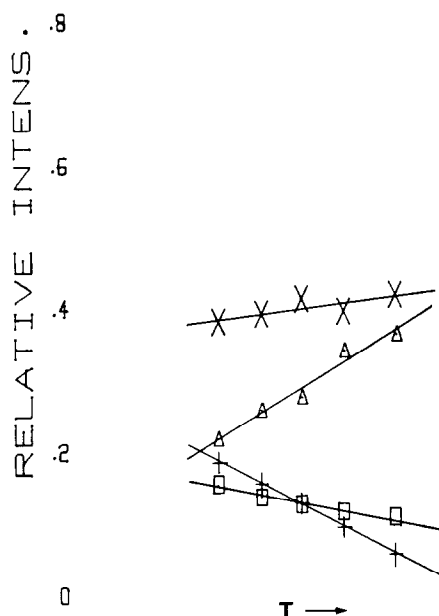


Fig. 5. Cyclobutanol (g),  $\nu(\text{OH})$ -Raman band:  $T$ -dependence of relative intensities of 4 components.

sent, e.g. *trans* and *gauche* OH conformations with equatorial and axial direction of the C–O bond, freezing of the thermalized mixture in the rare gas matrix would require freezing of *trans* and *gauche* OH-conformation and/or of the two conformations of the 4-ring. In principle, trapping of OH conformations appears possible. However, most attempts to freeze OH conformations systematically appear to have failed [9, 18] or the OH conformations appear to be subject to interconversion by near i.r. irradiation [10, 19–21]. With the cyclobutanol: Ar(s) system interconversion by i.r. irradiation ( $5000\text{--}200\text{ cm}^{-1}$ ) has not been observed in this work. Furthermore it should be remarked that model normal coordinate calculations for simple OH-conformations usually predict differences of normal frequencies of the order of  $10\text{--}30\text{ cm}^{-1}$  for different conformers (e.g. *syn* and *anti*, *gauche* and *trans*). Splittings of this magnitude have, however, not been observed in cyclobutanol: Ar(s) spectra. On the whole the existence of OH-conformers cannot be ruled out. Then there remains the possibility of at least two ring conformations. As mentioned in Section 1 Durig *et al.* [2] have proposed two ring conformations both featuring OH *gauche* conformation, but these have so far not been found in MW spectra. Recent extended *ab initio* calculations for cyclobutanol [12, 22] at the 4–31 G level predict no localized axial ring conformation, in contrast to Durig's assumption. Though *ab initio* calculations may not be reliable enough to rule out definitely the existence of localized axial ring conformations, they render these less probable.

The alternative explanation of matrix band profiles

as originating from sites is supported by the following experimental facts:

(i) the relaxation process of vibrational energy has been shown by direct experimental evidence to lead in some cases to sites differing from the site occupied before vibrational excitation [15];

(ii) thermal molecular beams often produce increasing linewidth with increasing source temperature;

(iii) by extended consistent force field calculations [23] it has been shown that the binding energy of surface atoms is of the order of  $< 1\text{ kcal mol}^{-1}$ , i.e. comparable with the translational thermal energy (1 degree of freedom) of the molecular beam. Since the latter varies from  $0.3\text{--}0.6\text{ kcal mol}^{-1}$  in going from  $300\text{--}600\text{ K}$ , it appears conceivable that higher energy sites may be created with increasing translational energy, both in Ar(s) and Xe(s).

Furthermore, the CFF model calculation has shown that the potential energy function of A:  $M_{K_M}$  systems (molecule A isolated in a matrix fragment with  $K_M$  rare gas atoms) possesses a wide variety of local shallow minima, leaving the possibility of a wide variety of substitutions of A into matrices differing only little with respect to energy and A–M interactions. As a matter of fact, complex lineshapes and splittings have been observed as a rule in matrix spectra, though up to now little quantitative study has been devoted to this problem. The analogy of line profiles in both Ar and Xe matrices lends some support to the site picture. Nevertheless it appears difficult to imagine the close correlation between the matrix band profiles and the band shape of the  $\nu(\text{OH})$  Raman band, cf. Figs 2 and 3, observed in this work.

The complex profile of the  $\nu(\text{OH})$  Raman band and its  $T$ -dependence as documented by Figs 2 and 5 may be understood in terms of a system of conformations in thermal equilibrium or else as a superposition of hot transitions related to the ring pucker motion, possibly combined with OH torsional transitions. Cyclobutanol appears to represent a case of a system with two finite degrees of freedom, which are strongly coupled by the kinematics of the pucker-internal rotation motion and by the potential energy function. This problem, together with *ab initio* calculations, will be analyzed in detail in a forthcoming paper.

A remark should be devoted to the observation of thermal decomposition of cyclobutanol mentioned in Section 2. Closer inspection of the decomposition products reveals that appropriately chosen temperature and residence time in the Knudsen cell allows nearly complete formation of  $\text{CH}_2:\text{CH}_2$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_2:\text{CHOH}$ . This offers a method to study the matrix spectra of the unstable species vinylalcohol.

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## REFERENCES

- [1] J. R. DURIG and W. H. GREEN, *Spectrochim. Acta* **25A**, 849 (1969).
- [2] J. R. DURIG, G. A. GUIRGIS, W. E. BUCY, D. A. C. COMPTON and V. F. KALASINSKY, *J. Mol. Struct.* **49**, 323 (1978).
- [3] J. N. McDONALD, D. NORBURY and J. SHERIDAN, *Spectrochim. Acta* **34A**, 815 (1978).
- [4] P. HUBER-WALCHLI and Hs. H. GUNTARD, *Spectrochim. Acta* **37A**, 284 (1981).
- [5] P. FELDER, T.-K. HA, A. M. DWIVEDI and Hs. H. GUNTARD, *Spectrochim. Acta* **37A**, 337 (1981).
- [6] M. SQUILLACOTE, R. S. SHERIDAN, O. L. CHAPMAN and F. A. L. ANETT, *J. Am. chem. Soc.* **97**, 3244 (1975).
- [7] H. FREI, T.-K. HA, R. MEYER and Hs. H. GUNTARD, *Chem. Phys.* **25**, 271 (1977).
- [8] J. MURTO, A. KIVINE and I. MITIKAINEN, *Chem. Phys. Lett.* **36**, 369 (1975).
- [9] C. E. BLUM, unpublished results.
- [10] J. MURTO and L. HALONEN, *Spectrochim. Acta* **34A**, 469 (1978).
- [11] P. GRONER, I. STOLKIN and Hs. H. GUNTARD, *J. Phys. E.* **3**, 261 (1970).
- [12] R. GUNDE, Ph.D. thesis, No. 7098, ETHZ (1982).
- [13] M. DUBS and Hs. H. GUNTARD, *Chem. Phys. Lett.* **64**, 105 (1979).
- [14] M. DUBS and Hs. H. GUNTARD, *J. Mol. Struct.* **60**, 311 (1980).
- [15] M. DUBS, L. ERMANNI and Hs. H. GUNTARD, *J. Mol. Spectrosc.* **91**, 458 (1982).
- [16] C. BAKER, I. P. COCKERILL, J. E. KELSEY and W. F. MADDAMS, *Spectrochim. Acta* **34A**, 673 (1978).
- [17] C. BAKER, P. S. JOHNSON and W. F. MADDAMS, *Spectrochim. Acta* **34A**, 683 (1978).
- [18] A. SERRALLACH, R. MEYER and Hs. H. GUNTARD, *J. Mol. Spectrosc.* **52**, 94 (1974).
- [19] H. FREI, T.-K. HA, R. MEYER and Hs. H. GUNTARD, *Chem. Phys.* **25**, 271 (1977).
- [20] R. T. HALL and G. C. PIMENTEL, *J. chem. Phys.* **38**, 1889 (1963).
- [21] J. POURCIN, G. DAVIDOVICS, H. BODOT, L. ABOUAF-MARQUIN and B. GAUTHIER-ROY, *Chem. Phys. Lett.* **74**, 147 (1980).
- [22] R. GUNDE, R. MEYER, T.-K. HA and Hs. H. GUNTARD, to be published.
- [23] R. GUNDE, P. FELDER and Hs. H. GUNTARD, *Chem. Phys.* **64**, 313 (1982).