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Laser Raman spectroscopy of NH_3 and ND_3 adsorbed on TiO_2(anatase)

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The adsorption of NH_3 and ND_3 on the anatase phase of TiO_2 has been studied using laser Raman spectroscopy. Peaks are observed due to OH (OD), NH_3 (ND_3) and NH_x (ND_x) species adsorbed on the oxide surface. Analysis of the isotopic shifts observed between adsorbed NH_3 and ND_3 together with G-matrix calculations, leads to the conclusion that one type of chemisorbed NH_3 is present on the surface, in contrast to previous studies suggesting the presence of two distinct types of chemisorbed NH_3. Evidence is also presented for adsorbed NH_x ($x = 1$ or 2) species formed by the dissociative adsorption of NH_3.

Keywords: Raman spectroscopy; ammonia; titania

1. Introduction

The surface properties of the anatase phase of TiO_2 are of interest owing to its use in a variety of catalytic applications. One of the more informative probes of the properties of an oxide surface is the adsorption of Lewis bases to characterize the surface acidity. In particular, NH_3 adsorption has been used extensively to characterize the surface of a number of oxides, including TiO_2 [1–6]. Recently, the use of TiO_2-supported V_2O_5 as a catalyst for the NO/NH_3 reaction has refocussed attention on the state of NH_3 adsorbed on TiO_2 [4,5]. On the basis of infrared spectroscopy (IR), it has been suggested that NH_3 bonds coordinatively to two different types of Lewis sites on the anatase surface [2–6]. Though numerous papers have addressed this system, disagreement regarding the assignment of the IR bands remains, as pointed out recently by Hino and Mikami [6].

In this communication, we report the results of laser Raman (LRS) studies of NH_3 and ND_3 adsorbed on anatase. The interpretation of these experiments, facilitated by G-matrix calculations, lead to the conclusion that only one type of chemisorbed NH_3 is present on the surface.

2. Experimental

The anatase phase of TiO_2, referred to hereafter as TiO_2(a), was obtained from $Ti(OH)_4$ formed by addition of titanium isopropoxide (Tyzar, Dupont) to a 1 : 1 water-isopropanol mixture at 268 K. After washing the solid several times to remove the isopropanol, it was dried in vacuum at 383 K overnight, then heated to 773 K in O_2 for 4 h. The phase of the resulting material was determined by LRS and X-ray diffraction to be ~ 95% anatase, ~ 5% brookite, with no detectable quantities of rutile. Chemical analysis placed the concentration of Fe, K, Cl, and Na impurities at < 50 ppm.

The system used to record the in situ Raman spectra is described in ref. [7]. Prior to adsorption, the TiO_2(a) was oxidized at 773 K for 1 h in purified O_2, cooled to 373 K and then purged for 1 h in He. NH_3 and ND_3 adsorbed onto the sample by passing a flow of He containing 0.5% ammonia through the cell for 0.5 h. Spectra were excited using the 488.0 nm line of an argon ion laser (Spectra Physics, Model 165), with the laser power at the sample set at 50 mW. The acquisition time used was 10 s per scan, and multiple scans were collected for ~ 1000 s. To cover the range from 200 to 4000 cm^{-1}, five separate spectra were collected and then merged. The average resolution was 6 cm^{-1}.

3. Results and discussion

The Raman spectra observed after the adsorption of NH_3 and ND_3 on TiO_2(a) at 373 K are shown in fig. 1, and the locations of the peaks detected are reported in table 1. Following NH_3 adsorption, narrow OH peaks are observed at 3663, 3675 and 3712 cm^{-1}, and peaks arising from adsorbed NH_3 are detected at 3394, 3350, 3315, 3265, and 3159 cm^{-1}. The positions of the peaks observed in fig. 1a are in excellent agreement with previous IR studies of adsorbed NH_3 [2–6]. The spectrum of adsorbed ND_3 is shown in fig. 1b. The peaks which appear at 2697, 2705, and 2735 cm^{-1} can be assigned directly to OD groups on the TiO_2(a) surface, formed by either the decomposition of ND_3, or by H/D exchange of ND_3 with OH groups. Adsorbed ND_3 gives rise to Raman peaks located at 2527, 2480, 2405, 2371, and 2313 cm^{-1} which are in excellent agreement with previous IR studies [6]. No peaks associated with adsorbed species were detected outside of the regions shown in fig. 1, indicating that the aforementioned peaks arise from NH_3 and ND_3 and not from impurities.

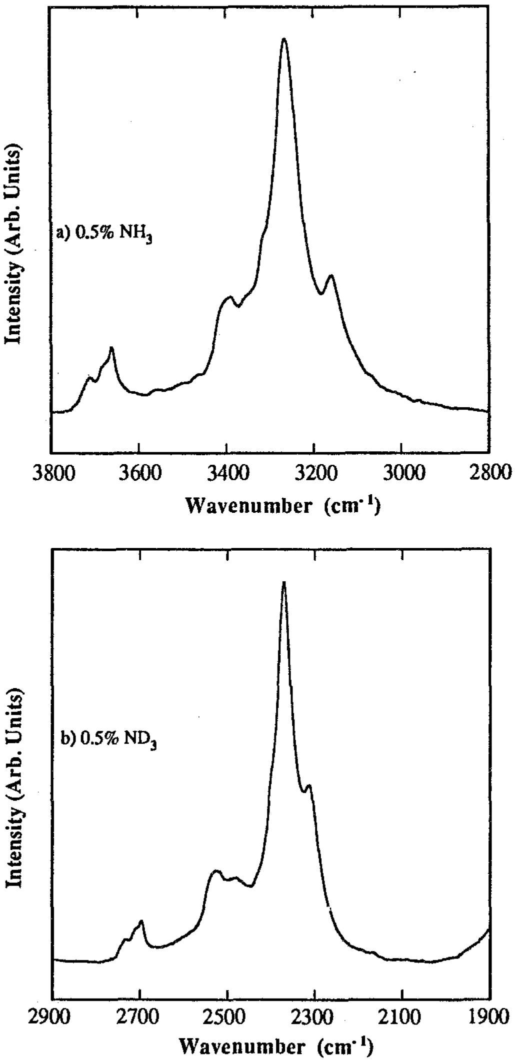

Fig. 1. Raman spectra of (a) NH_3; (b) ND_3 adsorbed on TiO_2(anatase) at 373 K.

The assignment of the bands observed in the vicinity of 3700 cm^{-1} and 2700 cm^{-1} to O-H and O-D vibrations, respectively, can be confirmed by looking at the ratio $\nu(H)/\nu(D)$. As shown in table 1, for the bands attributed to hydroxyl groups this ratio is 1.358, in good agreement with previous H/D exchange experiments of hydroxyl groups on oxides, which report a ratio of 1.355 [8].

Inspection of table 1 shows that excellent correlations exist between the ratio of $\nu(H)/\nu(D)$ for gas-phase and adsorbed NH_3, provided the 3265, 3394, and 3159 cm^{-1} peaks are assigned to the ν_1, ν_3, and $2\nu_4$ modes of adsorbed NH_3, respectively. For the 3265 and 3394 cm^{-1} peaks, the assignment to ν_1 and ν_3 modes agrees with previous assignments [2–6]. However, the assignment of the

Table 1
Isotopic shifts observed for the vibrational bands of adsorbed NH_3

Band assignment		Gas phase [a]		Adsorbed [b]	
		$\nu(cm^{-1})$	$\nu(NH_3)/\nu(ND_3)$	$\nu(cm^{-1})$	$\nu(NH_3)/\nu(ND_3)$
NH_3:					
A_1	ν_1	3336 (2420)	1.379	3265 (2371) 3315 (2405)	1.377 1.378
	ν_2	950 (748)	1.271	–	–
E	ν_3	3444 (2564)	1.343	3394 (2527)	1.343
	ν_4	1624 (1191)	1.364	3159 (2313) [c] 3188 (2340) [c,d]	1.366 1.366
NH_x:				3350 (2480)	1.351
OH:				3663 (2697) 3675 (2705) 3712 (2735)	1.358 1.359 1.357

[a] From ref. [9], with ND_3 values in parentheses.

[b] NH_3 adsorption on TiO_2 at 373 K, with ND_3 values in parentheses.

[c] Based on the $2\nu_4$ overtone of the adsorbed NH_3.

[d] From ref. [6].

3159 cm^{-1} band to a $2\nu_4$ vibration is in contrast to past work which attributed this feature to the ν_1 mode of a second type of chemisorbed NH_3 [2,3,6]. The ratio $\nu(H)/\nu(D)$ for the band at 3315 cm^{-1} is similar to that observed for the ν_1 gaseous NH_3 [9], and, hence, it is assigned accordingly. Also included in this table is a band at 3188 cm^{-1} observed by Hino and Mikami [6], which was assigned correctly to a $2\nu_4$ vibration. This band may be associated with the ν_1 peak located at 3315 cm^{-1}. The remaining NH feature at 3350 cm^{-1}, assigned previously to both ν_1 [1] and ν_3 [2–6] vibrations of NH_3, displays an isotopic shift which does not correlate with any of the modes of NH_3. Assignment of this band is discussed below.

The preceding discussion indicates that a good correlation exists between the isotopic shifts observed for gaseous NH_3 and NH_3 adsorbed on TiO_2(a), provided the peaks due to the adsorbed species are assigned as in table 1. More rigorous support for these assignments can be realized by comparing the observed shifts for the "harmonic" frequencies to those predicted by the product rule of Wilson [10]. This relationship is derived from an analysis of the normal modes of vibrations. The secular equation for the normal modes can be written as

$$|GF-\lambda I| = 0; \ \lambda = 4\pi^2c^2\omega^2 \tag{1}$$

where ω is the harmonic frequency of a normal mode, c is the speed of light, I is the indentity matrix, G is the kinetic energy matrix and F is the potential

Table 2
Analysis of the E symmetry species harmonics for NH_3

Band assignment	Gas phase			Adsorbed		
	$\omega_i(NH_3)$ [a]	$\omega_i'(ND_3)$ [a]	$\prod_i(\omega_i^2/\omega_i'^2)$ [b]	$\omega_i(NH_3)$ [c]	$\omega_i'(ND_3)$ [c]	$\prod_i(\omega_i^2/\omega_i'^2)$ [b]
ν_3	3577	2652		3525	2613	
ν_4	1691	1225	3.46	3360 [d]	2414 [d]	3.53
			$\frac{\lvert G_E\rvert}{\lvert G_E'\rvert}=3.50$ [e]			

[a] From ref. [9].

[b] See eq. (2).

[c] NH_3 adsorption on TiO_2 at 373 K, corrected for anharmonicity using constants in ref. [9].

[d] Based on the $2\nu_4$ overtone.

[e] The values used to evaluate the G-matrix were: $\alpha_{HNH} = 106.7°$, $m_H = 1.0081$ amu, $m_D = 2.0147$ amu, and $m_N = 14.0076$ amu [9].

energy matrix. All of the information regarding the force constants is contained in the F-matrix, while the G-matrix contains the reduced masses of the vibrating system. The invariance of the F-matrix to isotopic substitution reduces the secular equation to

$$\frac{|G|}{|G'|}=\frac{\prod_{i=1}^{n}\omega_i^2}{\prod_{i=1}^{n}\omega_i'^2} \tag{2}$$

where ω_i is the harmonic frequency of the ith normal mode of H-labeled species, and the primes correspond to D-labeled species. Provided the G-matrix is expressed in symmetry adapted coordinates, eq. (2) holds not only for entire block-diagonal G-matrix, but also for the sub-matrices corresponding to the individual symmetry species which make up the matrix. For the data obtained here, this relationship can only be tested for the E species, since the ν_2 mode required for the A_1 species is not observed. The observed Raman frequencies, corrected for anharmonicity using the experimental constants obtained by Benedict and Plyer [9], are shown in table 2. The agreement between the calculated value of eq. (1) (3.50) and that observed experimentally for adsorbed NH_3 (3.53) is excellent. In addition to confirming the assignments of the ν_3 and $2\nu_4$ vibrations, this analysis indicates that the anharmonicity of the vibrations of adsorbed NH_3 is not significantly different from that of gas-phase NH_3.

This analysis shows that the peaks located at 3394, 3265, and 3159 cm^{-1} following NH_3 adsorption on TiO_2(a) are due to the ν_3, ν_1, and $2\nu_4$ modes of an adsorbed NH_3 molecule. These peaks are all shifted down scale by ~ 70 cm^{-1} from the corresponding values observed for gas-phase NH_3, indicative of a strongly chemisorbed species [11]. The ν_1 mode located at 3315 cm^{-1} is characteristic of a more weakly bonded NH_3, since the frequency shift relative to the gas-phase is only ~ 20 cm^{-1}. Furthermore, the peak at 3315 cm^{-1} decreases in intensity relative to the peak at 3265 cm^{-1} with increasing adsorption temperature, consistent with the assignment of the former band to a more weakly bound NH_3 species [12]. Previous investigations of NH_3 adsorbed on TiO_2(a) have concluded that there are two distinct forms of chemisorbed NH_3 [2,6]. This was based on the attribution of the peak at 3159 cm^{-1} to the ν_1 mode of a second chemisorbed NH_3 species, shifted by 177 cm^{-1} from the gas-phase value. This conclusion is not supported by the present study, which shows that this peak is due to the $2\nu_4$ mode of adsorbed NH_3 associated with the ν_1 peak at 3265 cm^{-1}. As a result, only one type of chemisorbed NH_3 is suggested on the basis of this work.

The remaining feature located at 3350 cm^{-1} most likely arises from species formed by the decomposition of NH_3. Likely candidates for this species are NH_2 and NH groups, owing to similarity in location of the 3350 cm^{-1} peak with NH_2 groups adsorbed on Al_2O_3 $\{\nu_{as} = 3386, \nu_s = 3335$ $cm^{-1}\}$ [13], and NH groups adsorbed on Ni(111) $\{\nu_s = 3340$ $cm^{-1}\}$ [14] and Ni(110) $\{\nu_s = 3240$ $cm^{-1}\}$ [15]. The isotopic shifts can only be compared for NH species on Ni(111), for which a $\nu(H)/\nu(D)$ ratio of 1.35 was reported [14]. This agrees well with the value of 1.351 observed for the 3350 cm^{-1} peak. In addition, for model compounds containing NH groups, the $\nu(H)/\nu(D)$ ratio for the NH stretch of ND_2H $\{\nu_s = 3286$ $cm^{-1}\}$ is 1.352 [16], and the $\nu(H)/\nu(D)$ ratio for the NH stretch of HNSO $\{\nu_s = 3345$ $cm^{-1}\}$ is 1.349 [17]. Both of these values are close to 1.351, providing further evidence that the 3350 cm^{-1} band arises from adsorbed NH species. For NH_2 compounds, the isotopic shifts have been reported for the metal amide $NaAl(NH_2)_2$ $\{\nu_{as} = 3400, 3350$ cm^{-1}; $\nu_s = 3335, 3300$ $cm^{-1}\}$, which exhibits $\nu(H)/\nu(D)$ ratios of 1.363 and 1.343 for the symmetric and asymmetric modes, respectively [18]. The difference between these reported ratios and the ratio observed here of 1.351 is significant, indicating that the band at 3350 cm^{-1} does not arise from a C_{2v} symmetry NH_2 species. However, NH_2 groups with symmetry lower than C_{2v} cannot be ruled out, and hence the 3350 cm^{-1} peak is assigned to a surface NH_x ($x = 1$ or 2) species.

4. Conclusions

Laser Raman studies of adsorbed NH_3 and ND_3, combined with analysis of the G-matrix elements of the C_{3v} point group, have been used to clarify the assignments of the peaks arising from NH_3 adsorbed on TiO_2(anatase). In contrast to previous assignments, only one type of chemisorbed NH_3 is observed which is strongly coordinated to the TiO_2 surface. A weakly bound NH_3 is also seen, as evidenced by the smaller shift in frequency from the gas-phase.

Dissociative adsorption of NH_3 to form NH_x ($x = 1$ or 2) species is also observed.

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