Ti_2: Accurate Determination of the Dissociation Energy from Matrix Resonance Raman Spectra and Chemical Interaction With Noble Gases

Hans-Jörg Himmel* and Angela Bihlmeier[a]

Abstract: UV-visible and resonance Raman spectra of Ti_2 isolated in Ar, Kr, and Xe matrices at temperatures of 10 K were measured by using the 514 nm line of an Ar ion laser. The data show that the Ti_2 molecule interacts strongly with Xe, leading to a significant weakening of the Ti–Ti bond strength. The f(Ti–Ti) force constant decreases in the series Ar > Kr > Xe, from 232.8 Nm^{-1} in Ar and 225.5 Nm^{-1} in Kr to 199.7 Nm^{-1} in Xe. Additional experiments in an Ar matrix containing 2 % of Xe indicate the formation of a molecule of the formula Ti_2Xe. Our spectra for Ti_2 in an Ar matrix give evidence for several previously not observed members of the Stokes progression. The sum of experimental data allows for an improved estimation of the dissociation energy on the basis of a LeRoy–Bernstein–Lam analysis. A dissociation energy of 1.18 eV was derived from this analysis. The UV-visible data give evidence of the vibrational levels of an excited state of Ti_2.

Keywords: dissociation energy • matrix isolation • noble gases • Raman spectroscopy • titanium

Introduction

The precise description of weak multiple d–d bonding for elements in the first transition row still remains a challenge for theoreticians. Consensus seems now to be reached with respect to the question of the ground state of Ti_2, which is in all certainty $^3\Delta_g$.[1],[2] However, the energy differences between this ground state and three electronic states (e.g., $^1\Sigma_g^+$, $^3\Sigma_u^+$ and $^7\Sigma_u^+$) are very small. Accurate calculations of the relative energies of all these four states are made difficult due to the large effect of inner-shell (3s and 3p) correlation, which especially affects the $^1\Sigma_g^+$ and $^3\Delta_g$ electronic states. Surprisingly, there were, up to now, almost no calculations carried out for a quintet electronic state. MR-CI and ACPF calculations, with additional coupled-pair functional (MCPF) and contracted CI (CCI) calculations to estimate inner-core correlation, might be the most accurate calculations at hand to date. Some DFT calculations are also known.[3] However, these calculations have difficulties in yielding reliable values, for example, for the dissociation energies.

Experiments have shown that metal dimers generally are more reactive than metal atoms. Thus for example, Ga_2 has been shown to react spontaneously with H_2, while reaction of Ga atoms with H_2 requires photolytically induced excitation of the atom ($^2S \leftarrow {}^2P$ or $^2D \leftarrow {}^2P$ transition).[4],[5] This increased reactivity is caused by the presence of several excited electronic states with energies close to the electronic ground state; this allows a facile change of the electronic state. This change is often required for the reaction to proceed with a low activation barrier. In this respect a metal dimer can be used as a model for a cluster, the unusual reactivity of which can also be explained in this frame. Therefore, we have set out to study in more detail the differences in reactivity between dimers and atoms. Herein we report on the properties of a Ti_2 dimer, isolated at 10 K in different rare gas matrices (Ar, Kr, and Xe). It will be shown that Ti_2 interacts strongly with Xe, which has a significant effect on the Ti–Ti bond strength. In addition, our resonance Raman spectra allowed an accurate determination of the dissociation energy based on the method introduced by LeRoy, Bernstein, and Lam. The determination of the dissociation energy from resonance Raman data has the advantage over the third law (absolute entropy) method that the knowledge of the internuclear distance is not required. In other works, we are currently studying the reactivity of Ti atoms and Ti_2 dimers toward small model compounds like SiH_4 and SnH4.[6] Finally, our vibrationally resolved UV-visible spectra allow us to estimate the f(Ti–Ti) force constant in one of the excited states of Ti_2.

---

[a] Dr. H.-J. Himmel, A. Bihlmeier
Institut für Anorganische Chemie
Universität Karlsruhe
Engesserstrasse, Geb. 30.45
76180 Karlsruhe (Germany)
E-mail: himmel@chemie.uni-karlsruhe.de

DOI: 10.1002/chem.200305382

Experimental Section

Details about the matrix isolation method can be found elsewhere.[7] Very briefly, Ti metal was evaporated from a pure Ti filament with a diameter of 0.5 mm and a total length of the wire of 60 cm. The filament was connected to two water-cooled electrodes. A current between 4.2–5.6 A and a voltage between 7.0–10.0 V produced a relatively stable power of 35–45 W running through the wire during the 2 h of deposition. Hence the Ti vapor was deposited together with an excess of Ar or Xe onto a freshly polished Cu block kept at 10 K by means of a closed-cycle refrigerator (Leybold LB510). The Ar:Ti ratio was controlled by using a microbalance.

Resonance Raman spectra were recorded with the aid of a Jobin Yvon XY spectrometer with two pre-monochromators and a spectrograph (measurements in the subtractive mode) and equipped with a CCD camera (Wright Instruments, England). The 514 nm line of an Ar ion laser (Coherent, Innova 90) was used as excitation line. A resolution of 0.5 cm^{-1} was used in all measurements.

UV-visible spectra were recorded with a Xe arc lamp (from Oriel), an Oriel multispec spectrograph and a photodiode array detector. The spectra were taken with 0.2 and 0.5 nm resolution.

Results

UV-visible spectra: Figure 1 shows a UV-visible spectrum of Ti atoms isolated in an Ar matrix. In this experiment, the Ti filament was heated with 35 W (relatively low temperature), resulting in a matrix with a Ti:Ar ratio of approximately $1{:}10^5$, as estimated with a microbalance. The spectrum resembles that obtained previously by Gruen and Carstens.[8] All bands can be assigned to transitions of Ti atoms; there is no sign of any band due to Ti_2.

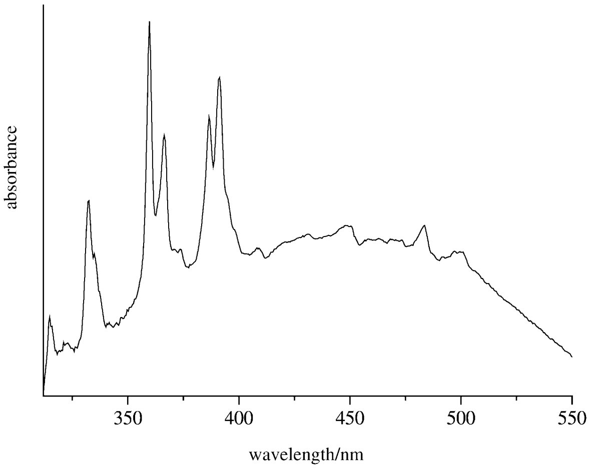

Figure 1. UV-visible spectra of Ti atoms isolated in a solid Ar matrix.

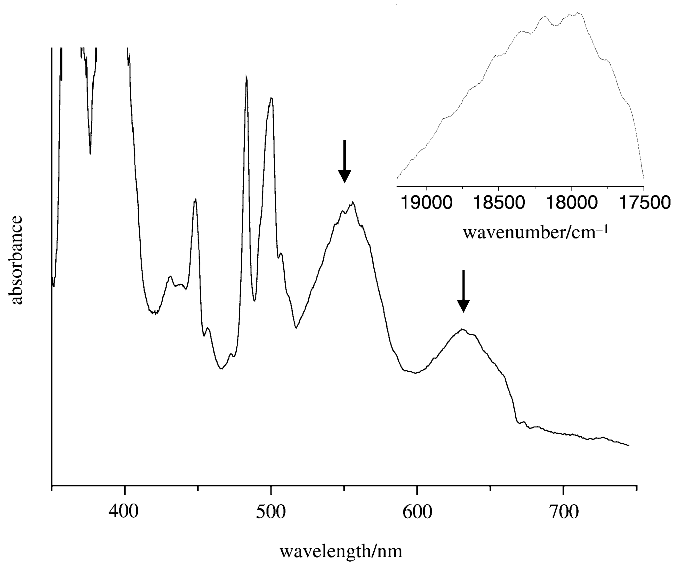

Figure 2. UV-visible sepctra of Ti atoms and Ti_2 isolated in a solid Ar matrix. Bands due to Ti_2 are marked by an arrow.

In Figure 2, a spectrum with increased Ti concentration is shown, achieved with a Ti filament operating at 40–45 W. Under these conditions, the concentration of Ti in the matrix is substantially higher (Ar:Ti ratio of ca. $1{:}\ 10^4$). As consequence, the bands due to Ti atoms gained in intensity. Two additional and broad absorptions, centered at 634 and 553 nm, were also detected; these were not present for low concentrations of Ti in the matrix. These two extra bands were assigned previously to Ti_2.[9] Our spectra give, however, for the first time evidence of a fine structure for the band centered at 553 nm. The area around this band was measured again with a better resolution (0.2 nm); the obtained spectrum is shwon in the inset in Figure 2. Maxima can be located at 17597, 17750, 17944, 18017, 18182, 18348, 18525, 18696, and 18880 cm^{-1}. The two maxima at 17944 and 18017 cm^{-1} are separated by not more than 73 cm^{-1}. It will be shown that two components of Ti_2 are present in the Ar matrix (see Raman spectra). Presumably, the doublet pattern arises from these two components. The separations between the maxima of the fine structure on the high energy side of this doublet amount to 166, 166, 178, 170, and 184 cm^{-1}.

The experiments were repeated, but this time in Xe as matrix host. Figure 3 shows the UV-visible spectra obtained at high Ti concentrations in Xe and Ar matrices. It can be seen that the two broad absorptions due to Ti_2 in Ar have

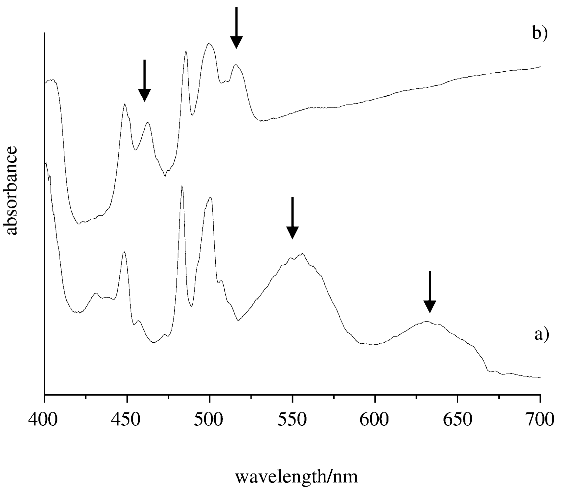

Figure 3. UV-visible spectra of Ti and Ti_2 isolated in a) a solid Ar and b) a solid Xe matrix. Bands due to Ti_2 are marked by an arrow.

disappeared. Instead, sharper bands show at 517 and 463 nm. If these bands belong to Ti_2, the Xe environment should interact strongly with the Ti_2 molecule. In the following, the Raman spectra taken for these matrices are shown, which give further insight.

Resonance Raman spectra: Figure 4 shows the resonance Raman spectra of Ti_2 isolated in a solid Ar matrix at 10 K. The conditions were the same as the ones used in the UV-visible experiments with high concentrations of Ti in the matrix. All members of the progression showed a complex band splitting with at least six clearly visible maxima of intensity. The distances between these maxima increased for the higher members of the progression. The fundamental mode was detected at 399.54, 401.62, 403.71, 405.79, 407.87, and 409.96 cm^{-1}, with the maxima at 405.79 and 403.71 cm^{-1} being the most intense ones. These values are in good agreement with those calculated previously for the $^3\Delta_g$ electronic state of Ti_2.[1] The first overtone showed at 794.92, 799.40, 802.88, 807.35, 811.82, and 815.79 cm^{-1}. The two bands at 807.35 and 802.88 cm^{-1} carried most of the intensity. Our measurements gave also evidence for signals at 1186.55, 1193,19, 1198.87, 1205.50, 1211.65, and 1217.79 cm^{-1} due to the second overtone, the most intense bands being the ones at 1205.50 and 1198.87 cm^{-1}. It followed a family of bands located at 1575.73, 1584.31, 1591.53, 1600.09, 1608.64, and 1617.17 cm^{-1}, of which the bands at 1600.09 and 1591.53 cm^{-1} were the most intense. This family can be assigned in all certainty to the third overtone. The forth overtone was most likely responsible for the features at 1961.40, 1972.14, 1981.15, 1992.28, 2002.55, and 2013.22 cm^{-1} detected in our spectra. Again two signals (the ones at 1992.28 and 1981.15 cm^{-1}) governed the scene. The fifth overtone can be assigned to the sharp Raman signals at 2380.54 and 2367.94 cm^{-1}, with clearly traceable satellites at 2344.70, 2357.35, 2393.12, and 2405.68 cm^{-1}. Number six in the series of overtones showed at 2724.63, 2739.35, 2751.71, 2766.37, 2780.60, and 2795.19 cm^{-1}, the maxima at 2766.37 and 2751.71 cm^{-1} being the most intense. Unfortunately, large fluorescence bands made it impossible to detect the following two overtones. However, the region between 3800 and 3900 cm^{-1} proved to be free of any strong fluorescence features and allowed the detection of the ninth overtone, which had maxima of intensity at 3847.52, 3867.54, 3905.43, 3884.89, 3924.93, and 3945.65 cm^{-1}, with those at 3905.43 and 3884.89 cm^{-1} carrying most of the intensity (see Table 1).

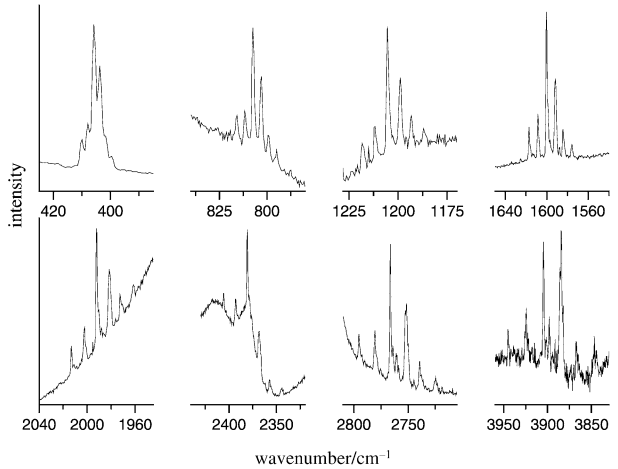

Figure 4. Resonance Raman spectra of Ti_2 isolated in an Ar matrix at 10 K. The spectra were measured with the 514 nm line of an Ar ion laser using a laser power of 10 mW. The resolution was 0.5 cm^{-1}.

Table 1. Observed signals [ν in cm^{-1}] of the $\nu(^{48}Ti{-}^{48}Ti)$ stretching mode and the members of the Stokes progression for Ti_2 isolated in Ar, Kr and Xe matrices at 10 K.

ν [cm^{-1}]	Vibrational quantum index
Ar matrix host	
403.71/405.79	0
802.88/807.35	1
1198.87/1205.50	2
1591.53/1600.09	3
1981.15/1992.28	4
2367.94/2380.54	5
2751.71/2766.37	6
3884.89/3905.43	9
Kr matrix host	
399.43	0
796.10	1
1190.02	2
1579.65	3
1968.08	4
2351.78	5
2733.38	6
Xe matrix host	
375.9/368.3	0
748.2/733.7	1

Additional experiments were performed with Kr as matrix gas. Most interestingly, the splitting of the Raman signals differed for Ti_2 in Kr to that observed in Ar matrices (see Figure 5a and b). Only one band of the ν (Ti–Ti) stretching fundamental dominated in intensity for Ti_2 isolated in Kr at 10 K. This band was located at 399.43 cm^{-1}. Satellites of the fundamental mode were traced at 395.26, 396.82, 401.0, and 403.08 cm^{-1} (see Figure 5b). In addition, weaker features at 796.10, 1090.02, 1579.65, 1968.08, 2351.78, and 2733.38 cm^{-1} appeared in the Raman spectra and can be assigned to overtones.[10] Also noteworthy is the small, but significant shift of the wavenumber to lower values in Kr.

To obtain more information, the experiment was repeated, but this time in a solid Xe matrix. The wavenumber of the ν(Ti–Ti) stretching fundamental now showed a pronounced shift toward smaller values (see Figure 5c). The fundamental and the first overtone exhibited, like the ones measured in an Ar matrix, a clear splitting into two components. These were located at 375.9 and 368.3 cm^{-1}, respectively, with shoulders on both sides of each component. The bands were somewhat broader than in the case of the Ar matrix. The first overtone was observed at 748.2/733.7 cm^{-1}.

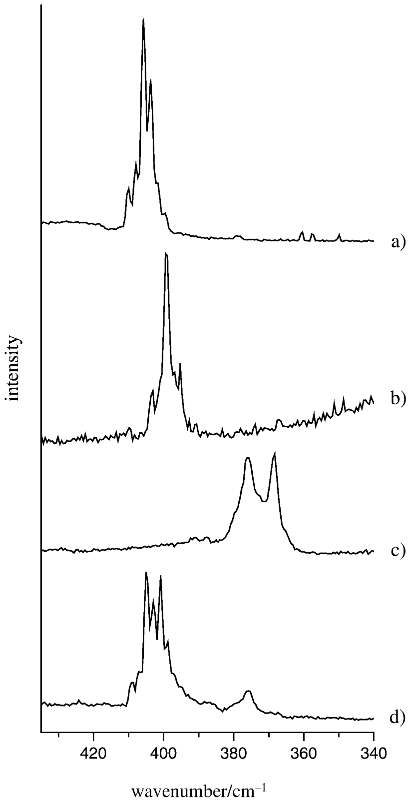

Figure 5. Comparison between the fundamental $\tilde{\nu}$(Ti-Ti) stretching mode of Ti_2 isolated in a) Ar, b) Kr, c) Xe, and d) 2% Xe in Ar. The very small and sharp features in a) in the region around 360 cm^{-1} are due to spikes ("cosmic events") in the spectrum rather than Raman scattering from the matrix.

Unfortunately, because of the increased half-width of the signals, no further member of the Stokes progression could be traced for Ti_2 isolated in a Xe matrix.[11]

Finally, experiments were conducted for Ti_2 in an Ar matrix that contained 2% Xe. In these experiments, a strong feature due to Ti_2 appeared at 400.84 and 404.49 cm^{-1}, with shoulders and weaker satellites at 396.68, 398.76, 402.93, 406.57, and 409.17 cm^{-1}. The splitting thus differs to the one in pure Ar, but the wavenumbers are similar. However, in contrast to the experiment in pure Ar, a second weaker band showed at 375.30 cm^{-1}, which can most likely be assigned to the same species as that responsible for the bands at 375.9 and 368.3 cm^{-1} in the experiments in pure Xe. Overtones of the ν(Ti–Ti) stretch of Ti_2 were also observed in these experiments. Members of the Stokes progression were detected at the following wavenumbers (in cm^{-1}): 806.27 (793.87, 797.84, 802.30, 810.23) for the first, 1204.55 (1191.80, 1198.41, 1211.15, 1217.27) for the second, 1599.02 (1566.17, 1574.28, 1581.94, 1590.48, 1607.09, 1616.06) for the third, 1990.18 (1957.61, 1967.91, 1979.48, 1986.33 (shoulder), 2000.43, 2010.66) for the forth, 2378.93 (2355.34, 2366.33, 2374.87 (shoulder), 2391.09, 2404.04) for the fifth, 2764.63 (2721.79, 2737.26, 2750.39, 2759.63 (shoulder), 2778.85, 2793.41) for the sixth, 3509.33, 3526.91 (and 3521.40) for the eighth (which was not observed in pure Ar because of the stronger fluorescence signals), and 3903.25, 3884.03 (3924.02, 3864.42) for the ninth overtone.

Discussion

UV-visible spectra: Our results are in good agreement with earlier accounts and indicate that the bands at 634 and 553 nm in the experiments carried out in Ar matrices are due to Ti_2. The observed intensities of the Raman signals are also in agreement with this assignment. Our spectra give for the first time evidence for a fine structure. This fine structure is most likely caused by Franck–Condon transitions into several vibrational levels of the excited state. Similar fine structures were observed, for example, in the case of Ni_2 isolated also in an Ar matrix. The separation of the maxima is approximately 170 cm^{-1}. Thus the excited state responsible for the band should have a ν(Ti–Ti) stretching mode of about 170 cm^{-1}. The Raman spectra show that the wavenumber of the ν(Ti–Ti) stretch for Ti_2 in its ground electronic state is approximately 404 cm^{-1}. As a consequence the force constant of the Ti–Ti bond drops from 232.8 N m^{-1} in the ground electronic state to not more than around 41 N m^{-1} in the excited state responsible for the band in the UV-visible spectra.

It might come as surprise that the two bands completely disappear when the experiments are performed in Xe instead of Ar. The new bands at 517 and 463 nm are likely candidates for Ti_2 in Xe. The differences of approximately 100 nm between the absorptions in Ar and Xe are very large. For example, shifts of about 20 nm were reported for CN radicals isolated in Ar and Xe matrices.[12] The large shift for Ti_2 implies a substantial change of the electronic properties. Because of the small energy differences between the different electronic states of Ti_2, it is plausible that the electronic state of Ti_2 changes in the course of the interaction with Xe. It will be shown that the results of the Raman experiments point to a relatively strong chemical interaction between Xe and Ti_2.

Resonance Raman spectra: The Raman spectra were recorded under resonance conditions. This implies that the laser line used in the experiments (514 nm) is close in energy to an electronic transition of Ti_2. The band around 553 nm detected in the UV-visible spectra is in all certainty this electronic transition. Because of the fine structure visible in the UV-visible spectra, we have also some information in hand of the excited state. In the experiments several fluorescence lines were detected and some of these signals can be attributed to Ti_2. The energy of the laser line is slightly higher than the energy required to electronically excite the Ti_2 molecules. Nevertheless, it is close enough to provide resonance conditions, the effect of which is an immense increase of the intensity of the Raman lines. This increase enabled the detection of several overtones.

As already mentioned, the signals show a complex structure with several maxima of intensity. This structure can partially be explained with the presence of the isotopes of Ti in their natural abundance. Figure 6 shows a simulation of the isotopic pattern for a Ti_2 molecule with the five Ti isotopes (^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, and ^{50}Ti) in their natural abundances. In this simulation, the $(^{48}Ti)_2$ isotopomer was centered at 405.79 cm^{-1} and the positions of all other 14 possible iso-

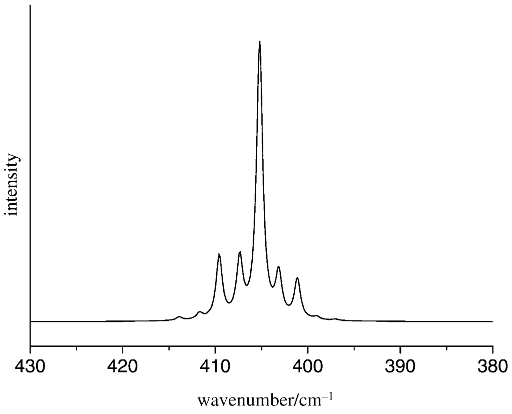

Figure 6. Expected isotopic pattern for Ti_2 (one component) with the five Ti isotopes in their natural abundance.

topomers were calculated on the basis of a harmonic potential. The half-widths of all Lorentzian-type functions were set to 0.5 cm^{-1}. It is evident that the experimentally observed pattern for Ti_2 in an Ar or Xe matrix (see Figure 2a and c) deviates from the expected one, while that observed for Ti_2 in Kr is in good agreement with the simulation. However, if one assumes the presence of two components of the $\nu(^{48}Ti-^{48}Ti)$ stretching mode (in the case of Ti_2 in Ar centered at 405.79 and 403.71 cm^{-1}), the observed pattern meets the expectation. The experiments in different matrix environments were informative concerning the nature of these two components. They indicate that the two components most likely arise from a splitting of the $^3\Delta$ electronic state of Ti_2 in the presence of the matrix environment. A previous suggestion to explain the two components can definitely be ruled out.[13] This previous line of argumentation includes the "accidental overlap of the most intense isotopic line of the $2''\leftarrow1''$ set and one of the less intense ones belonging to $1''\leftarrow0''$". However, this does not hold true for the following reasons:

1) The sum of the two components of the fundamental in Ar (403.71 and 405.79 cm^{-1}) does not coincide with the wavenumber of the first overtone (802.88 or 807.35 cm^{-1}); also, in the same vein, the sum of the wavenumbers of the two components of the fundamental mode in Xe amounts to 744.2 cm^{-1}, a value significantly smaller than the 748.2 cm^{-1} measured for one of the components of the first overtone.
2) The band splitting is completely absent in the case of Ti_2 in Kr and much larger for Ti_2 in Xe.
3) Most convincingly, the degree of splitting of the two components in an Ar matrix is affected by small quantities (2 %) of Xe in the matrix.

The ν(Ti–Ti) stretching fundamental experienced a 7 % reduction of its wavenumber by changing from Ar to Xe as the matrix host. It has been shown previously that the matrix environment can affect the position of the signal. This can be explained in some cases by a "solvation effect". For example, it has been shown that the difference of 23.5 cm^{-1} between the signal observed for InCl in the gas-phase and in a solid Ar matrix can be rationalized on the basis of a simple Onsager model.[14] However, in the case of Ti_2, the shift between the wavenumber in Ar and in Xe evidently cannot be explained on this basis. Therefore, one has to assume that the Xe atoms interact significantly with the Ti_2 molecule and this interaction leads to a reduction of the Ti–Ti bond strength. It is evident that Xe is more capable of interacting with Ti_2 than Ar or Kr. As a consequence, the force constant f(Ti–Ti) decreases from 232.8 N m^{-1} in Ar to 199.7 N m^{-1} in Xe. The clear inference is that this species is a molecule of the form Ti_2Xe or Ti_2Xe_n (n being a small number). Experiments with different concentrations of Xe in the matrix indeed argue for the formula Ti_2Xe. Quantum chemical calculations are currently being undertaken to get more information about a possible structure and the bond properties in such compounds. However, the variety of different electronic states in proximity to the ground state and the necessary inclusion of relativistic effects for Xe make reliable calculations very difficult.

It has been shown impressively in the last years that the reactivity of Xe is surprisingly high. Well-known examples featuring interactions between Xe and a transition-metal atom include the carbonyls $[XeM(CO)_5]$ (M = Cr, Mo, or W), for which a dissociation energy of approximately 0.63 eV was derived.[15] Very recently, complexes in which Xe interacts with a noble metal atom were discovered. Among these new compounds which were structurally characterized are the Au–Xe complexes $[AuXe_4][Sb_2F_{11}]_2$,[16] *cis*-$[AuXe_2(Sb_2F_{11})_2]$, *trans*-$[AuXe_2(SbF_6)_2]$, $[Au_2Xe_2(\mu\text{-}F)(SbF_6)_4]$, and *trans*-$[AuXe_2F(SbF_6)]$.[17] $[AuXe]^+$ and $[XeAuXe]^+$ were detected in the gas-phase by using mass-spectrometry[18] and theoretical calculations predict in the case of $[AuXe]^+$ a bond energy of as much as 1.30 eV and a bond length of 257.4 pm.[19] As to matrix work, the compounds HXeCCH, HXeCC (open shell species), and HXeCCXeH were generated and characterized lately in Xe matrices by UV-photolysis of acetylene and subsequent annealing at 40–45 K.[20] In the light of these recent discoveries it is reasonable that Xe interacts strongly with Ti_2. Future quantum chemical calculations will hopefully shed more light on the possible geometry of such a species. These calculations are a challenge for theoreticians, since they have to take account for inner-core correlation and relativistic effects.

Determination of the dissociation energy D_e: Figure 7 illustrates the increasing differences between the multiple of the wavenumber of the fundamental mode (harmonic potential approximation) and the observed values for the members of the Stokes progression of Ti_2 in Ar. Thus the anharmonicity is already substantial, especially for the ninth overtone. This experimentally observed anharmonicity is essential for the determination of the dissociation energy on the basis of the experimental results (see below).

Our determination of the dissociation energy relied on the formalism introduced by LeRoy, Bernstein, and Lam.[21] The actual potential near the dissociation can be approxi-

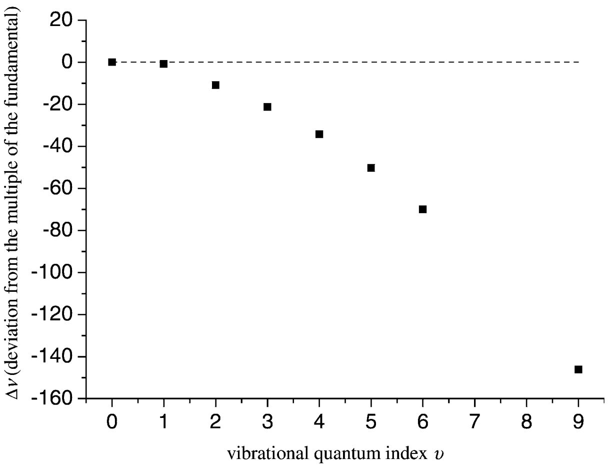

Figure 7. Differences between the multiples of the wavenumber measured for the ν(Ti–Ti) stretching fundamental and the wavenumbers measured for the members of the Stokes progression. The plot illustrates the anharmonicity of the Ti_2 potential.

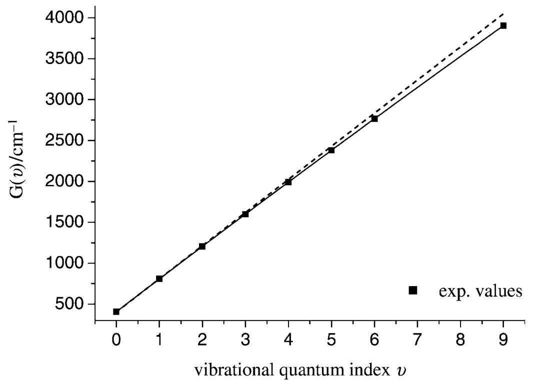

Figure 8. LeRoy–Bernstein–Lam analysis ("N_a expansion") for the observed members of the Stokes progression for Ti_2 isolated in an Ar matrix (see text for a detailed explanation). The dashed line illustrates the behavior in the harmonic potential approximation, for which the wavenumbers of the overtones are multiples of the one measured for the fundamental; however, this not harmonically corrected.

mately described by Equation (1), in which R is the atomic separation and n is determined by the nature of the long-range interaction.

$$V(R) \sim D_e - \frac{C_n}{R^n} \tag{1}$$

The power n is equal to six if induced-dipole–induced-dipole interactions dominate, and equal to five for quadrupole–quadrupole interactions. Thus n can be more or less readily obtained from the knowledge of the electronic states of the atomic dissociation products and (sometimes also) the identity of the molecular electronic state. Ti atoms exhibit a ^3F electronic ground state and Ti_2 dimers most likely have a $^3\Delta_g$ electronic ground state, and quadrupole–quadrupole interactions are expected to govern the scene near the dissociation limit. The parameter C_5 can be derived with the aid of interaction integrals tabulated by Chang ($C_5 = 4.158 \cdot 10^3\,cm^{-1}\,Å^5$).[22],[23] We have applied the method suggested by LeRoy and Lam ("N_a expansion") to interpolate between the formulas derived for the vibrational level energies near the dissociation limit (which result from a WKB treatment) and those that are closer to the bottom of the potential-energy curve. The vibrational level energies $G(v)$ can be approximately expressed in dependence of four parameters, which are the dissociation energy D_e, the noninteger effective vibrational index at the dissociation limit v_D, and the two expansion coefficients a_1 and a_2 [Eq. (2)]. $X_0(n)$ was previously calculated to be 0.1776 cm^{-1} for Ti_2.[23]

$$G(v) = D_e - X_o(n)(v_D - v)^{\frac{2n}{n-2}}\{1 + a_1(v_D - v) + a_2(v_D - v)^2\} \tag{2}$$

In Figure 8 the experimentally derived G(v) and v data points are fitted by using Equation (2). It can be seen that the fitted curve runs through all observed data points. A chi-square value of not more than 1.3 indicates that the "N_a expansion" reproduces nicely the observed trend. The values of the four parameters are: $D_e = 9470.7 \pm 178.9\,cm^{-1}$, $v_D = 39.99 \pm 0.52$, $a_1 = 0.0293 \pm 0.00007$, and $a_2 = (2.5 \pm 0.013)\,10^{-4}$. Thus, according to our results, the dissociation energy of Ti_2 amounts to 1.18 eV (113.9 kJ mol^{-1}). This result is in agreement to the previous estimate of $D_e > 1.05$ eV (although this estimate is, as shown above, partially based on a false assignment of the Raman signals).[23] Thus the Ti–Ti bond is comparably weak, somewhat weaker than the F–F bond (D^o(298 K) = 158.78 kJ mol^{-1}) in F_2[24] and also weaker than the Sn–Sn bond of Sn_2 (D^o(298 K) = 187.1 kJ mol^{-1}).[25] It is on the other hand stronger than the Na–Na bond in Na_2, for which a D^o(298 K) value of 73.60 ± 0.25 kJ mol^{-1} was derived.[24] With 133 ± 6 kJ mol^{-1}, the third-law estimate for D^o(298 K) of Al_2, based on resonant two-photon ionization spectroscopy,[26] comes close to the dissociation energy obtained for Ti_2.

Conclusion

Ti_2 was studied in Ar, Kr, Xe, and Xe/Ar matrices by means of UV-visible and resonance Raman spectroscopy. UV-visible spectra give evidence for two electronic transitions of Ti_2 and the detection of a vibrational fine structure, which allowed us to estimate the f(Ti–Ti) force constant in one of the excited states of Ti_2. Resonance Raman spectra were measured yielding the fundamental ν(Ti–Ti) mode and several overtones. On the basis of these results it was possible to determine the dissociation energy more accurately than in earlier accounts. An analysis following the method suggested by LeRoy, Bernstein, and Lam yielded a D_e value of 113.9 kJ mol^{-1} for Ti_2 in Ar.

Our experimental data clearly show that Ti_2 forms a relatively strongly bound complex Ti_2Xe with Xe. In this complex the Ti–Ti bond is significantly weakened with respect to free Ti_2. The UV-visible spectra are also strongly affected by the complexation. Future calculations should provide estimates of the geometry of this complex. These calculations are, however, a challenge for theoreticians. Ti_2 on its own has proved to be very difficult to calculate, owing to the presence of several energetically low-lying excited states. Calculations on Ti_2Xe have to take care of inner-core correlation and relativistic effects. Nevertheless we are optimistic that reliable calculations on this new interesting noble gas complex will be possible in the future.

Acknowledgment

The authors thank the Deutsche Forschungsgemeinschaft for financial support, Prof. Dr. W. Klopper for fruitful discussions, and B. Schucker and the mechanical workshop for their help with the construction of the Ti evaporator.

---

[1] C. W. Bauschlicher, Jr., H. Partridge, S. R. Langhoff, M. Rosi, *J. Chem. Phys.* **1991**, *95*, 1057.

[2] M. Doverstål, B. Lindgren, U. Sassenberg, C. A. Arrington, M. D. Morse, *J. Chem. Phys.* **1992**, *97*, 7087.

[3] See, for example: C. J. Barden, J. C. Rienstra-Kiracofe, C. Jonathan, H. F. Schaefer III, *J. Chem. Phys.* **2000**, *113*, 690.

[4] a) H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *Angew. Chem.* **2002**, *114*, 823; *Angew. Chem. Int. Ed.* **2002**, *41*, 796; b) H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *J. Am. Chem. Soc.* **2002**, *124*, 829.

[5] A. Köhn, H.-J. Himmel, B. Gaertner, *Chem. Eur. J.* **2003**, *9*, 3909.

[6] A. Bihlmeier, T. M. Greene, H.-J. Himmel, unpublished results.

[7] See, for example: H.-J. Himmel, A. J. Downs, T. M. Greene, *Chem. Rev.* **2002**, *102*, 4191.

[8] D. M. Gruen, D. H. W. Carstens, *J. Chem. Phys.* **1971**, *54*, 5206.

[9] R. Busby, W. Klotzbücher, G. A. Ozin, *J. Am. Chem. Soc.* **1976**, *98*, 4013.

[10] The higher members of the Stokes progression again showed the presence of two components (e.g. 1579.65/1577.84 cm^{-1} for the third overtone), which are thus likely to be present also in the fundamental, but separated by not more than 0.5 cm^{-1}.

[11] Additional experiments were conducted in N_2. However, the experiments failed to give any evidence of a band due to Ti_2. Instead, several strong fluorescence features appeared that are likely to belong to a spontaneously formed reaction product between Ti and/or Ti_2 and N_2.

[12] A. Thoma, G. Schallmoser, A. M. Smith, B. E. Wurfel, V. E. Bonybey, *J. Chem. Phys.* **1994**, *100*, 5387.

[13] C. Cossé, M. Fouassier, T. Mejean, M. Tranquille, D. P. DiLella, M. Moskovits, *J. Chem. Phys.* **1980**, *73*, 6076.

[14] H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 922.

[15] J. R. Wells, E. Weitz, *J. Am. Chem. Soc.* **1992**, 114, 2783.

[16] S. Seidel, K. Seppelt, *Science* **2000**, *290*, 117.

[17] T. Drews, S. Seidel, K. Seppelt, *Angew. Chem.* **2002**, *114*, 470; *Angew. Chem. Int. Ed.* **2002**, *41*, 454.

[18] D. Schröder, H. Schwarz, J. Hrusak, P. Pyykkö, *Inorg. Chem.* **1998**, *37*, 624.

[19] P. Pyykkö, *Science* **2000**, *290*, 64.

[20] L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, M. Raesaenen, *J. Am. Chem. Soc.* **2003**, *125*, 4696.

[21] See, for example: R. J. Le Roy, W.-H. Lam, *Chem. Phys. Lett.* **1980**, *71*, 544.

[22] T. Y. Chang, *Rev. Mod. Phys.* **1967**, *39*, 911.

[23] T. L. Haslett, M. Moskovits, A. L. Weitzman, *J. Mol. Spectrosc.* **1989**, *135*, 259.

[24] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.

[25] K. Pak, M. F. Cai, T. P. Dzugan, V. E. Bondybey, *Faraday Discuss. Chem. Soc.* **1988**, *86*, 153.

[26] Z. Fu, G. W. Lemire, G. A. Bishea, M. D. Morse, *J. Chem. Phys.* **1990**, *93*, 8420.

Received: July 25, 2003
Revised: October 13, 2003 [F5382]